Versatile Routes for Acrylonitrile Butadiene Rubber Latex Hydrogenation

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

The direct catalytic hydrogenation of acrylonitrile-butadiene-rubber in latex form was studied for the development of a simple process for the modification of unsaturated diene-based polymers.

Acrylonitrile-butadiene-rubber, known as NBR, is a rubber synthesized from acrylonitrile and butadiene (monomers) via copolymerization. It has been widely utilized as oil resistant rubber components in industry. Selective hydrogenation of the residual carbon-carbon double bonds (C=Cs) in the NBR backbone could improve its physical and chemical properties which greatly extend its range of application and lifetime. However, the current hydrogenation procedure involves a number of cumbersome steps which substantially increase the production cost. Hence, it is worthwhile developing new technology which HNBR could be synthesized in a cheaper and environmentally friendly way.

Considerable efforts have been undertaken to realize this goal. Among them, hydrogenation of commercial NBR latex becomes especially attractive and promising. Direct hydrogenation of NBR in the latex not only avoids using large amounts of organic solvent which is required in polymer solution hydrogenation but also produces hydrogenated-NBR (HNBR) in the latex form which can be utilized for painting or coating.

It has been reported that the commercial NBR latex could successfully be hydrogenated using $RhCl(PPh_3)_3$ with added triphenylphosphine (PPh_3). High quality HNBR latex was obtained after the reaction. However, the hydrophobicity of $RhCl(PPh_3)_3$ and PPh_3 greatly restrict their separation and diffusion in the NBR latex, resulting in a very low activity in the heterogeneous NBR latex system.

In order to improve the process of NBR latex hydrogenation using the $RhCl(PPh_3)_3/PPh_3$ catalytic system, an in-situ hydrogenation process was developed where $RhCl(PPh_3)_3$ was directly synthesized from the water-soluble catalyst precursor $RhCl_3$ and PPh_3 in the NBR latex. The catalyst precursor $RhCl_3$ is soluble in the aqueous phase of the NBR latex and PPh_3 was well dispersed in the aqueous NBR latex after adding small amounts of alcohol. Compared with using pre-made solid catalyst, the in-situ synthesized catalyst in the NBR latex could quickly be transported into the polymer particles and faster hydrogenation reaction was observed. In addition, the influence of various operational conditions on the hydrogenation rate; such as catalyst concentration, latex system composition, reaction temperature and hydrogen pressure have been studied.

With the success of NBR latex hydrogenation using $RhCl(PPh_3)_3$ catalyst, two water-soluble analogs of $RhCl(PPh_3)_3$, $RhCl(TPPMS)_3$ (TPPMS = Monosulfonated Triphenylphosphane) and $RhCl(TPPTS)_3$, (TPPTS = Trisulfonated Triphenylphosphane) were then used for NBR latex hydrogenation. It was found that the difference of their solubility in water greatly affected their activities in NBR latex hydrogenation. Successful hydrogenation was achieved using the $RhCl(TPPMS)_3$ catalyst while only low conversion was observed when using the $RhCl(TPPTS)_3$ catalyst. The catalysts retention in the polymer is also in agreement with the reaction results. High conversion could only be achieved when the catalyst diffused into the polymer particles in the latex. Using the $RhCl(TPPMS)_3$, the reaction could be carried out in a temperature range of 70 ℃ to 120 ℃. And no co-catalyst ligand (i.e. TPPMS) was required for catalyst diffusion or reaction. In addition, the effects of the particle size of the NBR latex and the molecular weight of NBR (gel fraction) on hydrogenation were also investigated using lab made “in-house” NBR latices. It was found that the hydrogenation reaction was much faster with smaller particle size. It was also observed that the gel fraction in the latex particles greatly influenced the mobility of the polymer chains within the particles.

In addition to the rhodium based catalysts, ruthenium based catalysts have also been investigated for NBR latex hydrogenation. With the recent findings of the hydrogenation activity of the Grubbs type

metathesis catalyst, the hydrogenation of NBR latex was studied first using the second generation of Grubbs catalyst (G2). It was found using the G2 catalyst with small addition of organic solvent such as mono-chlorobenzene (MCB) to dissolve the catalyst resulted in a successful hydrogenation in NBR latex. Meanwhile, the metathesis activity of the G2 catalyst was also measured during the hydrogenation reaction. Comparing with conventional ruthenium catalysts, the multifunctional G2 catalyst benefited the NBR latex hydrogenation process by controlling its molecular weight change. The increase of molecular weight within hydrogenation reaction was partially offset by a synchronous metathesis reaction between NBR and the added of chain transfer agent (CTA). As a result, no visible gel was observed in the final HNBR product. In addition, the kinetic behavior of the hydrogenation was systematically studied with respect to the catalyst concentration, hydrogen pressure as well as NBR concentration. The apparent activation energy over the temperature range of 80-130 ℃ for the hydrogenation of metathesized NBR was also measured.

Further experiments showed that the second generation of Hoveyda-Grubbs catalyst (HG2) could be employed for the NBR latex hydrogenation even without adding any organic co-solvent to dissolve the catalyst. Although HG2 catalyst is insoluble in water, it could be well dispersed in aqueous system with the addition of certain surfactants. A fast catalytic hydrogenation (e.g. TOF > 7000 h^{-1} at 95 mol.% conversion) was achieved and successful hydrogenation was still observed under very low catalyst concentration. Compared with using G2 catalyst, the degree of metathesis reaction under HG2 in this organic solvent free process was very limited.

As a result of this research project, different catalysts were successfully developed for hydrogenation of NBR in latex. A significant milestone was achieved in improving polymer hydrogenation technology.

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Dedication

To the memory of Dr. Jialong Wu

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Nomenclature

ACN:	Acrylonitrile
ABS:	Acrylonitrile-butadiene-styrene
ASTM:	American standard test method
Conv.:	Conversion
CTA:	Chain transfer agent
DTAC:	Dodecyltrimethylammonium chloride
FT-IR:	Fourier transform infrared
HEXNa:	$Ph_2P-(CH_2)_5-CO_2Na$
HNBR:	Hydrogenated nitrile butadiene rubber
ICP-OES	Inductive coupled plasma-optical emission spectroscopy
KPS:	Potassium persulfate ($K_2S_2O_4$)
MCB:	monochlorobenzene
MEK:	Methyl ethyl ketone (2-butanone)
^1H NMR:	Proton Nuclear Magnetic Resonance
NBR:	Acrylonitrile butadiene rubber (Nitrile rubber)
NR:	Natural rubber
Os:	Osmium
PB:	Polybutadiene
PPh_3:	Triphenylphosphine
psig:	lb/in^2
rpm:	Rotation per minute
Rh:	Rhodium

Ru:	Ruthenium
SOA:	Sodium oleate acid
SBR:	Styrene Butadiene Rubber
SDS:	Sodium dodecyl sulfate
THF:	Tetrahydrofuran
TON:	Turn over number
TPPMS:	Monosulphonated triphenylphosphine
TPPTS:	Trisulphonated triphenylphosphine

Chapter 1

Introduction

1.1 General introduction to polymer hydrogenation

Diene polymers are a type of polymer synthesized from monomers which contain two carbon-carbon double bonds (C=Cs), such as butadiene, isoprene and chloroprene. Diene-based polymers usually include these diene polymers (e.g. polybutadiene, polyisoprene) and those copolymers of which at least one monomer is a diene (e.g. acrylonitrile-butadiene copolymer, styrene-butadiene copolymer). A common feature of the diene-based polymers is the presence of the olefinic structure within the polymer. Right now, diene-based polymers are some of the most important commercial polymers (rubbers). Their usefulness to scientists and engineers comes not only from their desirable physical properties, but also because they may be used as a base polymer for a variety of chemical modification reactions.

The chemical modification of diene-based polymers is an important research area in polymer chemistry [1, 2]. It can provide polymers with desirable physical and chemical properties which are not accessible by standard polymerization techniques [3]. The chemical modification via hydrogenation of the C=Cs in these polymers has been extensively examined. It has exhibited special importance in extending the ranges of application for unsaturated polymers.

Generally, hydrogenated polymers show improved thermal and oxidative stability. For example, hydrogenated styrene-butadiene-styrene copolymer, i.e. Kraton G® (Shell), exhibits excellent weatherability and improved thermal, oxidative and UV stability [4]. This polymer has been used in laminating films, high performance adhesives, and sealants. The hydrogenated acrylonitrile-butadiene rubber (HNBR), i.e. Therban® (Lanxess, Germany), Zetpol® (Zeon chemicals, Japan), has been used in seals, hoses, and belts for automobiles and in oilfield applications due to its excellent thermal stability and improved resistance to oil and chemicals [5, 6]. Hydrogenated polystyrene (HPS) and polycyclohexylethylene [7, 8], exhibit enhanced thermal and oxidative stability, as well as excellent optical properties, and have been proposed for use in optical application.

1.2 The significance of acrylonitrile butadiene rubber hydrogenation

Acrylonitrile butadiene rubber, known as NBR, is a synthetic polymer which is produced via copolymerization of acrylonitrile and butadiene. It is a typical diene-based polymer which is widely used in industry as an oil-resistant elastomer. Recent developments especially in the automotive industries as well as in the field of oil exploration and processing require the polymer to possess high temperature stability and long-time oil resistance to aggressive surroundings. Although some special elastomers such as fluoro-elastomers (FKM) and fluoro-silicone (FMQ) were considered, theses elastomers are quite pricy. Hydrogenated NBR has emerged as the most promising elastomer by demonstrating a unique combination of excellent mechanical properties, good oil resistance, high-temperature performance as well as reasonable price, which fills the void between the expensive high-performance elastomers and general purpose NBR.

1.3 The commercial technology for manufacturing HNBR

So far, several approaches have been developed to hydrogenate polymers. The most prevalent method for producing HNBR is to hydrogenate the polymer using molecular hydrogen (H_2) with a catalyst in organic media. Based on the solubility of the catalyst in the reaction medium, the catalytic hydrogenation reaction could be mainly divided into two processes: (i) a homogeneous process and (ii) a heterogeneous process. The homogeneous process uses a well-defined organometallic complex as a catalyst (in some circumstances, a co-catalyst ligand needs to be added additionally in order to keep the activity of the catalyst). The catalyst could be dissolved in the reaction medium (i.e. polymer solution) and well contacted with the C=C bonds in the NBR. Hence, complete C=C bond hydrogenation can be achieved after the reaction. However, the separation of the catalyst as well as the co-catalyst ligand from a highly viscous polymer solution is very costly and time-consuming.

The heterogeneous process uses supported catalysts. These catalysts are immiscible with the polymer solution. As a result, hydrogenation reaction only occurs at the surface of the catalyst. Different from homogeneous process, the separation of the catalyst in heterogeneous process is much easier. However, due to the kinetic limitations, a high catalyst loading is required when using heterogeneous catalyst. In addition, catalyst leaching to the product is also inevitable.

1.4 Direct hydrogenation of NBR latex

Although catalytic hydrogenation of NBR is still being utilized for the production of HNBR, it involves cumbersome pre-preparation and post-treatment (e.g. obtaining solid NBR from the latex, dissolving the solid rubber in a large amount of organic solvent, recovering solvent and catalyst and coagulating the hydrogenated polymer). These steps substantially increase the cost of HNBR and limit its large scale application.

NBR is synthesized via emulsion polymerization and is available in the form of latex. It is obviously attractive to directly hydrogenate NBR in latex form. Such a process would avoid using large amount of organic solvent which is required for conventional hydrogenation. In addition, it provides extra advantages in minimizing the negative impact on the environment as well as reducing production costs. Considerable efforts have been made to realize direct NBR latex hydrogenation. However, the complexity of the polymer latex system (the existence of many additives such as chain transfer agent and anti-oxidant) and the requirement from industry for high levels of hydrogenation (at least 95 mol.% hydrogenation of total C=Cs without severe gel) makes NBR latex hydrogenation much more difficult.

The most successful example of NBR latex hydrogenation was developed by Rempel et al. by using Wilkinson's catalyst, $RhCl(PPh_3)_3$ in the presence of added triphenylphosphine (PPh_3) [9]. Under such a catalytic system, high quality HNBR latex (no-gel formation) could be obtained [9, 10]. However, compared to the NBR solution hydrogenation, the reaction in the latex system was much slower.

1.5 Scope of this research

Hence, the motivation of this research is to further improve the direct hydrogenation of NBR latex using the $RhCl(PPh_3)_3/PPh_3$ catalytic system and to develop new efficient catalysts which could be used in NBR latex hydrogenation. First, in order to improve the dispersion of Wilkinson's catalyst in the aqueous system, the key of this success is to find such a system that the Wilkinson's catalyst can be easily dispersed in water (hydrophilic) and quickly diffuse into the NBR micelles (hydrophobic). As we know, $RhCl_3$, the most common rhodium salt used as a rhodium source for catalyst synthesis, is highly soluble in water and can be preferably adopted for the in-situ synthesis of water-soluble rhodium catalysts. Since the in situ synthesis requires a shorter synthesis time and very small volumes of the different synthesis reagents, making it cost effective for in-situ synthesis of $RhCl(PPh_3)_3$ from $RhCl_3$ and PPh_3 in the NBR latex, this method was developed for NBR latex hydrogenation. The hydrogenation reaction results were studied and compared with those obtained from using the pre-made solid $RhCl(PPh_3)_3$ catalyst.

With the success of the in-situ synthesized $RhCl(PPh_3)_3$, two kinds of water-soluble rhodium complexes, $RhCl(TPPMS)_3$ and $RhCl(TPPTS)_3$, were synthesized and tested for direct NBR latex hydrogenation. It was found that the NBR latex hydrogenation could be successfully achieved using the RhCl(TPPMS)$_3$ catalyst while little conversion was observed when using the RhCl(TPPTS)$_3$ catalyst. The catalysts retention in the polymer is also consistent with the reaction results. High conversion could only be achieved when the catalyst diffused into the polymer particles in the latex. The effects of the reaction parameters such as temperature, pressure, catalyst loading were also investigated. Meanwhile, in house NBR latices were synthesized via emulsion co-polymerization of acrylonitrile and butadiene providing different particle sizes and were also used for NBR latex hydrogenation. It was found that in house NBR latex could be successfully used for NBR latex hydrogenation.

Ruthenium carbene complexes are well-known catalysts for metathesis reactions. In the last decade, researchers have also found that these catalysts showed activities towards hydrogenation reaction. Therefore, we attempted to hydrogenate NBR in latex form using these ruthenium catalysts. First, we studied the Grubbs second generation catalyst (G2) in NBR latex system. Generally the G2 catalyst is insoluble and could not be easily dispersed and transported as a hydrophobic catalyst complex in the aqueous latex system. Therefore tiny amount of organic solvent was added to dissolve the catalyst. It was observed that the NBR could be hydrogenated using the G2 catalyst and that NBR metathesis degradation was also achieved.

By screening several commercial available Grubbs type catalysts; we discovered that the Hoveyda-Grubbs second generation catalyst (HG2) could be successfully employed for the NBR latex hydrogenation even without adding any organic co-solvent to dissolve the catalyst. It was found the HG2 catalyst could be well dispersed in the aqueous system with the addition of a surfactant. An exceptionally fast catalytic hydrogenation (TOF > 7000 h^{-1} at 99 mol.% conversion) could be achieved under the HG2 catalyst and this hydrogenation is still feasible under very low catalyst concentration. Therefore many pre/post-treatment procedures are no longer necessary which makes this process very promising and robust, but simple.

Chapter 2

Literature Review: Hydrogenation of polymers, direct hydrogenation of polymer latex and the catalyst recovery

2.1 Introduction

This chapter begins with a short review of conventional polymer hydrogenation in polymer solutions together with recent versatile novel polymer hydrogenation technology. It then focuses on one of the most promising polymer hydrogenation technologies: the direct hydrogenation of unsaturated polymers in polymer latex. Different methods for latex polymer hydrogenation are summarized and compared with respect to their hydrogenation efficiencies and limitations. Among them, the research status on NBR latex hydrogenation is specifically emphasized. Engineering issues in polymer latex hydrogenation such as separation of catalysts and cross-linking of polymer chains are also briefly discussed. Research methodology and approaches (Chapter 3) for the hydrogenation of NBR latex will be generated based on an analysis of the literature.

2.2 Diene-based polymer and its hydrogenation

Diene-based polymers are an important branch of polymers which is extensively utilized as industrial rubbers or elastomers. The common feature of these polymers is that they all have unsaturated C=C double bonds in the polymer chains. For industrial applications, a limited amount of these double bonds are advantageously used for vulcanization, while the remaining large quantities of double bonds have disadvantages in that they reduce the polymer resistance to weathering, oxidation, and ozone attacks. Such disadvantages become more evident when these polymers are used as thermoplastic elastomers, modifiers and transparent impact-resistant materials such as styrenic resins and olefinic resins, or when they are used in solvents/oils/high-temperature environments.

Hydrogenation of the C=C bonds in polymer chain is an important approach to alleviate this disadvantage. The resultant polymers usually exhibit special chemical and physical properties which the precursor polymers do not possess. With a lower level of un-saturation in the polymers, their physical properties such as tensile strength, elongation, thermal stability, light stability and solvent resistance might be changed. For example, the removal of the C=C units in polybutadiene (PB) provides a tough semi-crystalline polymer similar to linear polyethylene or an elastomer such as poly(ethylene-*co*-butylene), depending on the relative levels of units with 1,2 or 1,4 structure. Hydrogenation of a styrene-butadiene-styrene triblock copolymer (SBS) with a moderate amount of 1,2-addition units in the center block yields a copolymer with a poly-(ethylene-*co*-butylene) center segment which is greatly increased in its thermal and oxidative stability, together with improved processability and serviceability at higher temperature. Hydrogenation of acrylonitrile butadiene rubber results in its tougher and more stable derivative, hydrogenated nitrile butadiene rubber (HNBR). Depending on the acrylonitrile content and the degree of hydrogenation, HNBR exhibits better physical and mechanical properties including high tensile strength, low permanent set (especially at high temperatures), very good abrasion resistance and high elasticity [6]. It also shows excellent thermal and chemical stability towards heat and demonstrates better properties at low temperatures (lower brittle point) than other heat- and oil-resistant elastomers (Figure 2-1). Hence, it is now widely used for timing belts in cars, due to its good static as well as dynamic properties at under-the-hood operation temperatures, and it also exhibits good retention of properties under continuous heat exposure. In addition, new grades of the material with improved low-temperature flexibility are extending the HNBR service temperature range, allowing new applications in seals and mounts. For example, HNBR is also proving useful for seals and moldings of motor car engines that run on new fuels such as bio-diesel. Seal applications also include air conditioner O rings, shock absorbers, power steering systems and water pumps. HNBR has also been widely used in industrial seals for oil field exploration and processing, as well as rolls for steel and paper mills.

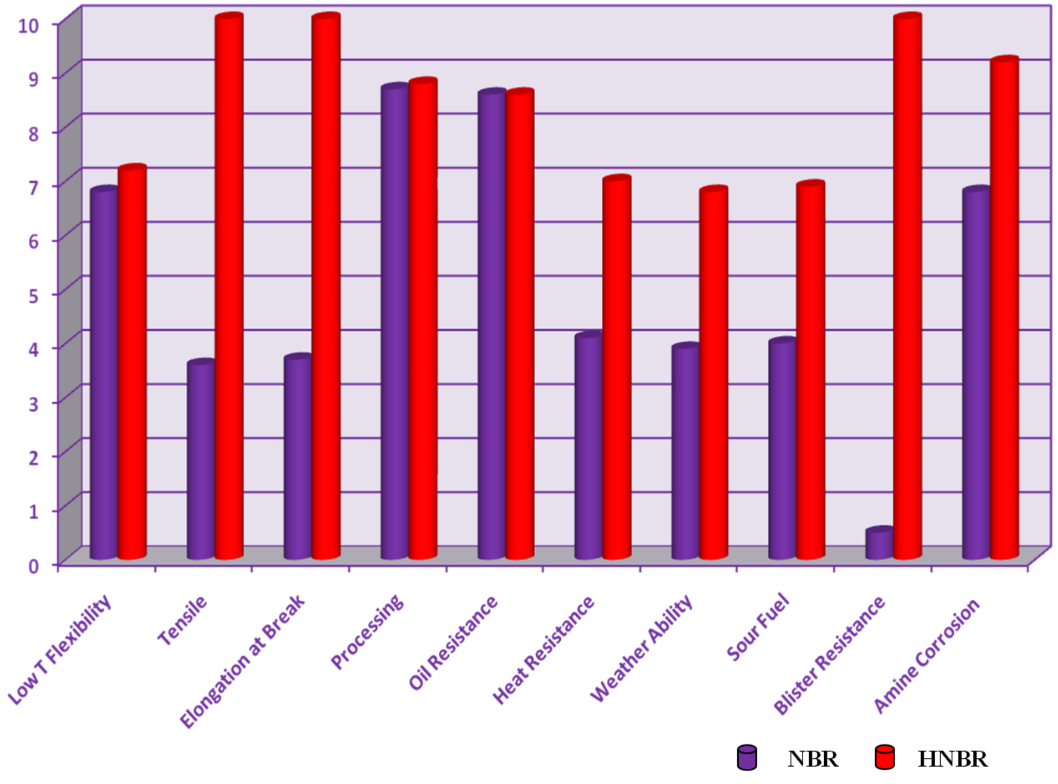


Figure 2-1 Properties of HNBR vs. NBR

2.3 Conventional polymer hydrogenation technology

Hydrogenation is a well-established technology for post-polymerization chemical modification of polymers. Polymer hydrogenation presently is carried out using a variety of techniques in polymer solutions. Basically, there are two approaches to hydrogenate polymers in polymer solutions: non-catalytic route and catalytic route. The major difference between these two approaches is whether a catalyst is involved in the hydrogenation reaction or not.

The conventional polymer hydrogenation in polymer solution has been comprehensively reviewed by several authors [1-3, 11]. Hence, it will be briefly described here and the development of NBR hydrogenation will be discussed as a case study of polymer hydrogenation.

2.3.1 Non-catalytic hydrogenation route

The non-catalytic hydrogenation is carried out using a hydrazide precursor, such as *p*-toluenesulfonyl hydrazide (TSH) [12]. At elevated temperature (e.g. 110 to 160 ℃), TSH could thermally decompose and form diimide (N_2H_2) in-situ. The reactive diimide adds hydrogen atom across the C=C double bond and releases N_2. This method circumvents the use of high-pressure equipment and expensive catalysts, but the stoichiometric diimide hydrogenation reaction is not suitable for large scale production. Besides, people have also found it promotes cis-trans isomerization of 1,4-dienes and polymer chain scission and cyclization during the hydrogenation which deteriorates the quality of the final polymer product [13].

2.3.2 Catalytic hydrogenation route

In a catalytic route, the polymer hydrogenation reaction is triggered by the catalyst. Until now, numerous catalysts have been developed for hydrogenating conjugated diene based polymers and these catalysts are classified into two types: heterogeneous catalysts and homogeneous catalysts.

Polymer hydrogenation using heterogeneous catalysts began from early 1950s. Significant efforts were made to use heterogeneous catalysts for the hydrogenation of polymers. Heterogeneous catalysts are composed of active metal or metals supported on porous material which has a large surface area. They are insoluble in the polymer solution. First, the polymer to be hydrogenated is dissolved in a suitable solvent, after which the polymer is brought into contact with hydrogen in the presence of a heterogeneous catalyst. During hydrogenation of the polymer, the contact between the polymer and catalyst is difficult due to the influence of the high viscosity of the reaction system and the influence of steric hindrance of the polymer chains. Meanwhile, the reacted polymer also tends to remain on the surface of the catalyst which interferes with subsequent access to active centers of the catalyst with the un-reacted polymer. Although the separation of catalyst from heterogeneous catalytic systems is usually easy, the strong adsorption of the polymer onto the heterogeneous catalyst makes it difficult to completely remove the catalyst from the hydrogenated polymer solution. The low reaction rates and the catalyst leaching into the polymer product can be impediments in the heterogeneous hydrogenation technology.

The discovery of homogeneous catalysts for polymer hydrogenation occurred later than heterogeneous catalysts. However, due to their higher activity and superior selectivity than the heterogeneous counterparts, polymer hydrogenation research on homogeneous catalysts was quickly developed later on. A critical review specifically on polymer hydrogenation using homogeneous catalysts has recently been published [2]. Homogeneous hydrogenation utilizes a metal complex (organometallic) as the catalyst. The reaction using a homogeneous catalyst is similar to that using a heterogeneous catalyst except that both the polymer and catalyst could be dissolved in the organic solution which makes them well contacted. Therefore, compared to the heterogeneous catalyst, the homogeneous catalyst generally exhibits higher activity under the same reaction temperature. In addition, homogeneous catalysts has a well defined catalyst structure which makes it possible to hydrogenate the conjugated diene portion of a copolymer of a conjugated diene without affecting other reducible function groups (e.g. nitrle, benzyl or carbonyl group) in the polymer structure. Compared to heterogeneous catalyst, the disadvantage of homogeneous catalysis is also distinctly.

From 1960s till now, various catalysts have been tested on polymer hydrogenation. To our knowledge, the number of effective heterogeneous catalysts for hydrogenating polymers is limited. Among them, palladium based catalysts showed the best activity and selectivity.

Compared to heterogeneous catalysts, different types of homogeneous catalysts could be used in polymer hydrogenation, including 1) Ziegler-type catalysts obtained from an organic acid salt or acetylacetone salt of nickel, cobalt, iron, or chromium which reacts with a reducing agent such as an organic aluminum compound; 2) Metallocene complexes; 3) Organometallic catalysts based on VIIIB precious metals.

2.3.3 The development of NBR solution hydrogenation

Among all of the hydrogenated elastomers, HNBR is the most commercially significant. The NBR hydrogenation technology was first developed by Nippon Zeon using a supported Palladium catalyst. 5 wt.% palladium on carbon was first employed and only 47 mol.% hydrogenation was obtained under this catalyst [14]. By modifying the reaction conditions and particle size of the carbon support, the hydrogenation conversion significantly improved. Further improvements in the catalytic activity were demonstrated by 1) adding co-catalyst/promoters such as calcium [15], aluminum [16] or lithium acetate [17]; 2) changing the support e.g. carbon black [18], silica [18], alkaline earth carbonate [19], $CaCO_3$ [20] and TiO_2 [21].

The use of homogeneous catalysts for the hydrogenation of NBR was first patented by Bayer A.G. [22-24]. Among the investigated catalysts, Wilkinson's catalyst [$RhCl(PPh_3)_3$], is considered as the most preferable for the hydrogenation of NBR as it provides high selectivity towards the olefin double bonds with minimized cross-linking problems. Some other Rh based complexes such as $RhH(PPh_3)_4$ [25], $Rh(PPh_3)_2$(COD)(p-toluene sulfonate) [26] are also excellent catalysts for NBR solution hydrogenation. The most important concern for using the rhodium catalyst is its relatively high cost.

Metal complexes based on other VIIIB group elements were studied for NBR hydrogenation. Parent et al. described the selective hydrogenation of C=C within NBR using the homogeneous catalyst precursor, $OsHCl(CO)(O_2)(PCy_3)_2$ in solution, which has a high hydrogenation activity for hydrogenation of NBR [27]. However, this catalyst is not as effective as Wilkinson's catalyst in suppressing the polymer crosslinking problem, which tends to occur during the later stages of hydrogenation. Ruthenium-based catalysts have also been used for the hydrogenation of NBR [28-33]. Compared with the osmium-based catalyst, the ruthenium based catalysts are efficient but are more susceptible with respect to causing cross-linking in NBR during the hydrogenation. Bimetallic catalyst comprising rhodium and ruthenium was also used for the hydrogenation to order to combine the high selectivity of the rhodium complex with the lower cost of the ruthenium complex [34]. It was found the catalytic activity of the bimetallic complex catalyst system was similar to that of the single rhodium-complex catalyst, containing the same total amount of metal.

2.4 Novel technology for polymer hydrogenation

Although metal-catalyzed hydrogenation reaction in polymer solution has been utilized for the production of hydrogenated polymers (e.g. NBR, SBR), a large amount of organic solvent is required and the separation of the hydrogenation catalyst from the polymer causes the price of these polymer materials to be quite high, which has substantially limited their large scale application. The direction of research on polymer hydrogenation is now focused on developing new reaction media. Using new reaction media may avoid the addition of organic solvent thus making the hydrogenation process more environmental-friendly.

2.4.1 Polymer hydrogenation in the solid state

Hydrogenation of polymer in the bulk form was first reported in 1989. Gilliom developed the catalytic hydrogenation of polystyrene-block-polybutadiene-block-polystyrene (PS-PB-PS) and 1,2-polybutadiene (1,2-PB) in bulk form using polymer entrapped Wilkinson's catalyst

$RhCl(PPh_3)_3$ or Crabtree catalyst $Ir(COD)(PMePh_2)_2PF_6$ [35]. Homogeneous catalysts were selected for this study becuase of their potential for diffusion into the polymer. The catalyst was introduced into the polymer by dissolving the polymer and catalyst together in an organic solvent and then the organic solvent was removed by evacuation. The hydrogenation reaction was performed under 0.7-3.0 Mpa hydrogenation pressure at 60 ℃. The hydrogenation reaction occurred and up to 90 mol.% conversion was obtained. However, the low mobility of the catalyst within the polymer matrix makes the reaction rate quite slow.

To improve the catalyst diffusion in polymer matrix, Li et al. studied on the bulk hydrogenation of NBR entrapped with the Wilkinson catalyst under supercritical CO_2. Different reaction times, reaction temperatures, hydrogen pressures and loadings of the catalyst as well as the thicknesses of the polymer films was systematically investigated [36]. It was found that CO_2 could help in improving the transport behavior of catalyst in the polymer matrices and the hydrogenation reaction rate was greatly increased.

Rempel et al. developed a new route to hydrogenate NBR in the bulk form by simply mixed bulk NBR particles (average 1 cm in diameter) with $RhCl(PPh_3)_3$ catalyst. The hydrogenation was performed at elevated temperature (e.g. 145 ℃). It was found that high conversions could be achieved in a few hours [37].

2.4.2 Polymer hydrogenation in ionic liquid

Souza et al. synthesized a dialkyl-imidazolium ionic liquid mixture and used it as an inexpensive solvents for the biphasic hydrogenation of poly(acrylonitrile-butadiene) rubber (NBR) catalyzed by $RuHCl(CO)(PCy_3)_2$ [38]. Meanwhile, MacLeod et al. systematically studied the hydrogenation of polybutadiene (PBD), nitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR) in a toluene/*N,N′*-butylmethylimidazolium tetrafluoroborate, ($BMI^+BF_4^-$) system with a water-soluble rhodium catalyst, $RhCl(TPPTS)_3$ (TPPTS = triphenylphosphine, trisulfonated) [39]. The catalyst shows high conversion (94 mol.%) with PBD, while only low conversions were observed for NBR and SBR hydrogenation.

2.4.3 Direct polymer latex hydrogenation

Many natural and synthetic elastomers are available in the form of aqueous latices or emulsions e.g. natural rubber latex (NRL), emulsion styrene-butadiene rubber (E-SBR), and acrylonitrile butadiene rubber latex (NBRL). In the latex, the small polymer particles are suspended in an aqueous solution. Thus, direct hydrogenation of these polymers in the latex form could avoid the dissolution process involved in preparing a polymer solution hydrogenation which requires a large amount of organic solvent.

2.4.3.1 Catalytic hydrogenation with water-insoluble catalyst

Homogeneous catalysts which are effective for polymer solution hydrogenation have been used for polymer latex hydrogenation. To mix the hydrophobic catalyst with the aqueous latex, usually the catalyst was dissolved an organic solvent and then dispersed in the aqueous latex. In most of experiments, the organic solvents used for dissolution of the catalyst were also good solvents for the polymers. Hence, the solvents could also swell the polymer particles in the latex, making the double bond more accessible to the catalyst.

Krause hydrogenated SBR latex using $RhCl(PPh_3)_3$. In this case, the catalyst is dissolved in benzene and the benzene-SBR latex mixture with 1.65 wt.% dispersion of SBR (67:33 volume ratio) was hydrogenated at 4.0MPa at room temperature [40]. More than 99 mol.% C=C bonds in SBR could be reduced in 18 h. Murrer et al. studied the hydrogenation of acrylonitrile-butadiene-styrene (ABS) emulsion using $RhCl(PPh_3)_3$ [41]. An ABS emulsion was first diluted with water and then mixed with the catalyst acetone/toluene solution. At the end of the reaction, two layers were observed. The catalyst stayed within the organic layer while the ABS emulsion remained in the aqueous layer.

Kubo et al. hydrogenated NBR latex using a benzene solution of palladium acetate as catalyst [21]. The catalyst solution was mixed with the aqueous latex under a 3:1 volume ratio in order to maintain the stability of the emulsion. The hydrogenation reaction was carried out at 3.0MPa and 50 ℃ for 6 hours. More than 90 mol.% hydrogenation conversion could finally be achieved.

Guo et al. developed two processes for the selective hydrogenation of the C=C bonds in NBR latex in the presence of a number of ruthenium catalysts [42]. One of the processes was carried out in a homogeneous system. The organic solvent methyl ethyl ketone (MEK) which is miscible with the NBR latex and can dissolve the polymer and catalyst was used. The other process was performed in a heterogeneous system. The organic solvent chlorobenzene which is immiscible with the NBR latex phase but still can dissolve the polymer and catalyst was used. In both processes, quantitative hydrogenation of the C=C bonds of the NBR latex was achieved in the presence of $RuCl_2(PPh_3)_3$ catalyst. The hydrogenation conversion can be more than 95 mol.% at 150 ℃ within 4 hours. The author also found that the addition of certain types of additives (e.g. ferrous ammonium sulfate, carboxylic acid) could minimize the cross-linking side reaction under the Ru-based catalysts.

Yao et al. reported that over 82 mol.% conversion was reached for NBR hydrogenation in latex form based on a patented process involving a Rh-Ru bimetallic complex [34, 43]. Organic solvent acetone/mono-chlorobenzene (MCB) was added to the aqueous latex as a co-solvent.

Dersch et al. invented a method to hydrogenate the unsaturated C=C double bonds in styrene-butadiene-rubber (SBR) emulsion [44]. This inventive method is characterized by integrating the hydrogenation catalyst into an aqueous dispersion of SBR without adding any solvent. Ruthenium

(III) tris-2, 4-pentaketone was added into the monomer mixture before emulsion polymerization to produce the SBR emulsion and tri-n-butylphosphine was added into the SBR emulsion. After stirring the emulsion, hydrogen was introduced and a 95 mol.% hydrogenation conversion was achieved using their method.

Most recently, Rempel reported that NBR latex could successfully be hydrogenated by $RhCl(PPh_3)_3$ with the addition of triphenylphosphine [45]. Although $RhCl(PPh_3)_3$ catalyst is insoluble in water, the catalyst was slowly dissolved in the melted PPh_3 droplets under the reaction temperature (> 130 ^{o}C). The melted droplet containing catalyst then diffused into the NBR particles to trigger hydrogenation [10].

2.4.3.2 Catalytic hydrogenation with water-soluble catalyst

In the last 20 years, increasing interest in catalytic reactions in aqueous media has focused on developing water-soluble transition metal complexes because of the avoidance of organic toxic solvents, providing substantial environmental and economical benefits. The use of water soluble analogs of Wilkinson catalyst i.e. $RhCl(TPPMS)_3$ and $RhCl(TPPTS)_3$ have been the subject of significant interest for many years. These catalysts are successfully used in the biphasic hydrogenation/hydroformylation of small olefins since they offer the advantages of easy separation of the products and recycle of the catalyst [46, 47].

Meanwhile, different kinds of water-soluble catalysts have also been studied for the hydrogenation of different polydiene latices. Papadogianakis et al. studied the hydrogenation of polybutadiene-1,4-block-poly(ethylene oxide) and polybutadiene using Rh/TPPTS in aqueous micelles with the surfactant dodecyltrimethylammonium chloride (DTAC) [48]. It was found that the activity of the catalysts decreases dramatically with increasing molecular weight of the reactants.

Singha et al. studied on NBR latex hydrogenation using the water soluble catalyst $RhCl(DPM)_3$ (DPM = diphenyl phosphino benzene *m*-sulphonate) [49]. The hydrogenation of the NBR latex was carried out over a large range of pressure, temperature and catalyst concentration. However, the industrially required high conversion could not be achieved and the hydrogenation reaction was accompanied by an increase in gel content of the HNBR. By elevating the temperature and hydrogen pressure, the degree of hydrogenation increased but the gel content remained almost invariant. The reasons for the insolubility of HNBR prepared using the water soluble catalyst was not clearly understood.

Mudalige and Rempel studied the hydrogenation of polybutadiene (PBD), styrene-butadiene (SBR) and nitrile butadiene (NBR) polymers in aqueous/organic biphasic media catalyzed by the water-soluble complex $[RhCl(HEXNa)_2]_2$ (HEXNa = $Ph_2P\text{-}(CH_2)_5\text{-}CO_2Na$) [50]. The hydrogenations were carried out on the polymer emulsions formed by suspending a polymer solution in distilled, deionized water. The hydrogenation conversion obtained after 6 hours was about 53 mol.% at 100 ℃ and 5.5 MPa. However, the catalyst was extracted into the organic phase during the reaction.

Yasuhiko et al. hydrogenated NBR latex using a $RhCl(TPPTS)_3$ catalyst [51]. The hydrogenation reaction was performed under 0.8 MPa hydrogen pressure at 60 ℃ for 24 hours. The latex obtained after the hydrogenation reaction was stable but the highest reported hydrogenation conversion was only 56 mol.%.

2.4.3.3 Non-catalytic techniques for hydrogenation of polymer latex

A non-catalytic technique using diimide (N_2H_2) reduction of C=C bonds has also been applied to saturate the diene-based polymer latex. Diimide acts as a mild reducing agent for a variety of symmetrical unsaturated bonds [52]. Although diimide could be generated under different ways, the oxidation of hydrazine using hydrogen peroxide is the method most commonly utilized to produce diimide in-situ in the aqueous phase for polymer latex hydrogenation. Wideman first used diimide for NBR latex hydrogenation in 1984 [53]. After that, different research groups systematically studied NBR latex hydrogenation under a hydrazine-diimide route in the presence of boric acid [54], cupric ion [55] or selenium [56].

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

2.5 Other issues in polymer hydrogenation

2.5.1 Catalyst recovery

In the development of new catalytic hydrogenation processes, separation of catalysts is important. Efficient separation of catalysts to enable their reuse for subsequent cycles of reactions is a key challenge. Several fundamental approaches have been summarized to propose a solution to the catalyst separation problem [57, 58].

Precipitation of the catalyst from polymer solutions can be accomplished by treating the polymer solution with different additives like acid/base and/or oxidants. Other similar methods to precipitate catalysts from the polymer solutions include contacting the polymer solution with a trialkyl aluminum compound in the presence of water [59], treating the polymer solution with a chelating resin which is comprised of iminodiacetate ions [60], bubbling oxygen/nitrogen in the presence of an aqueous solution of an acid [61], reacting with an aqueous solution of ammonia and carbon dioxide [62], and contacting the polymer solution with an aqueous solution of a weak acid followed by contacting it with an aqueous solution of a weak base [63].

Adsorption is commonly used for catalyst removal or recovery. This process involves treating the polymer solution with suitable materials which adsorb the catalyst residue and are then removed by filtration. Panster et al. proposed a method involving adsorbers made from organo siloxane copolycondensates to recover rhodium and ruthenium catalysts from solutions of HNBR [64]. They claimed that the residual rhodium could be reduced to less than 5ppm. Right now, the rhodium-based catalyst residues from HNBR solution are removed by using an ion-exchange resin with different functional groups like thiourea, present on a resin which is both macro-porous and mono-dispersed [65].

Weiss et. al. developed a method to separate the Ni colloid catalyst from HNBR latex [66]. They cooled down the mixture and then added a complexing agent to adsorb the catalyst and coagulate the latex. The metal remained as a metal salt in the serum.

Several aqueous biphasic catalytic systems using super critical CO_2 have been developed with the catalyst immobilized in the water layer. These systems are truly biphasic ($scCO_2$/liquid) in nature and have been mainly applied for hydrogenation reactions [67, 68]. One report disclosed enhanced catalyst reactivity and separations using water/carbon dioxide emulsions or micro-emulsions [69, 70]. 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. A new inverted biphasic catalysis system using supercritical CO_2 as the stationary catalyst phase and water as the continuous phase was reported for the Rh catalyzed hydroformylation of polar substrates [71]. Product separation and catalyst recycling is possible without depressurizing the autoclave.

2.5.2 Crosslinking in polymer hydrogenation

Although the mechanism of crosslinking during hydrogenation of diene based polymers is not well understood, 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 Ruthenium catalysts. Rempel et al. speculated a Michael-type addition mechanism to account for this problem [72, 73]. An NBR latex was hydrogenated in methyl ethyl ketone (MEK) at 2.5 to 10.0 MPa hydrogen pressure and 100 to 200 ^{o}C. Organic additives such as ascorbic acid, chloroacetic acid, hydroxyl acetic acid and phenoxy acetic acid were added in the reaction. The additives had a beneficial effect in minimizing the gel content.

Belt reported that cross-links can be broken by adding some chemicals such as phenylhydrazine [74] and Wang et al. found that the mass fraction of gel in the hydrogenated NBR was significantly reduced by adding hydroquinone [75].

2.6 Conclusions

Hydrogenation of polymers offers great potential to modify their properties. Hydrogenated diene-based polymers, especially, hydrogenated NBR have been demonstrated to provide high performance materials for a wide spectrum of applications.

Catalytic hydrogenation of polymers holds much promise for preparing novel polymeric materials that cannot be synthesized by direct polymerization alone. Development of proper catalysts and understanding of the hydrogenation mechanism remains an important area in polymer hydrogenation. Hydrogenation of polymers in solution has been studied by many groups. Kinetic models based on proposed hydrogenation mechanisms have been reported and been found to fit the experimental results very well. On the other hand, the mechanism of hydrogenation of polymers in latex is still the subject of much speculation. A full understanding of the latex hydrogenation mechanism and the development of corresponding kinetic models will facilitate the design of hydrogenation processes and the design of catalysts for polymer hydrogenation. Hence, further investigation on the hydrogenation of polymer latex is still of much interest to academic and industrial researchers.

Hydrogenation of latex elastomers has been reported in the literature involving the dispersion of oil soluble catalysts with organic solvents, by using water soluble catalysts or by using the non-catalytic diimide reduction process.

When oil soluble catalysts were used, there was a general consensus 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 can be hydrogenated in the latex form to a high degree of hydrogenation. Using water-soluble catalysts may eliminate the need of organic solvents for dissolution of catalyst. However, from the previous results presented above, the low final hydrogenation conversion and the gel formation are the two major problems associated with water soluble catalysts.

Recently, an important discovery is that $RhCl(PPh_3)_3$ catalyst with PPh_3 as a catalytic system for NBR latex hydrogenation. The reactions were achieved without the addition of any organic solvent. This is the first time that the direct catalytic hydrogenation of acrylonitrile-butadiene rubber latex has been successfully realized in the absence of any organic solvent with a conversion of higher than 95 mol.% without cross-linking of the polymer.

Chapter 3

Research Methodology and Approaches

3.1 Introduction

The motivation in research is to optimize the current catalytic process for NBR latex hydrogenation using the $RhCl(PPh_3)_3/PPh_3$ catalytic system and/or develop new efficient processes for NBR latex hydrogenation by exploiting efficient catalytic systems. In the long term, we are aiming at a diene-based polymer latex hydrogenation process which is more environmentally friendly and economical.

3.2 Objectives

Hydrogenation of NBR latex has been achieved by using $RhCl(PPh_3)_3$ catalyst with added PPh_3. However, several critical issues are still existed in this current process. One major concern is the efficiency of catalyst for NBR hydrogenation in latex form. Therefore, the direction of this research project is to improve the hydrogenation efficiency. In addition, it is also important to exploit new catalytic systems which could be used for NBR latex hydrogenation.

The objective of new hydrogenation process should be:

1) Improving the hydrogenation reaction efficiency for the $RhCl(PPh_3)_3/PPh_3$ catalytic system;

2) Developing a new catalytic system for NBR latex hydrogenation and achieve the industrially required hydrogenation conversion with high reaction rate.

In addition, the stability of the latex as well as the occurrence of cross-linking side reactions should be concerned.

3.3 Research Goals

3.3.1 Optimization of the current NBR latex hydrogenation process

It is known that NBR latex can be hydrogenated by using the $RhCl(PPh_3)_3$ catalyst in the presence of PPh_3. A starting point for this hydrogenation is to increase the hydrogenation efficiency (reaction rate) using this. The major issue in this process is to improve the diffusion of the hydrophobic catalyst in the aqueous NBR latex.

3.3.2 New catalyst exploration

It is also important to explore other catalyst to see if it could be used for the hydrogenation of NBR in latex form. As the hydrogenation reaction is carried out in aqueous media, some water-soluble catalysts were used. The most prevalent method to synthesize water soluble catalyst from conventional catalyst is to modify the catalyst ligand. Therefore, water soluble analog of $RhCl(PPh_3)_3$ catalysts, $RhCl(TPPMS)_3$ and $RhCl(TPPTS)_3$ were synthesized and used in NBR latex hydrogenation.

It has been reported ruthenium, osmium or iridium based organometallic complexes could catalyze NBR hydrogenation reaction. These catalysts are investigated for NBR latex hydrogenation.

3.3.3 Quality of HNBR from NBR latex hydrogenation

In many cases, hydrogenation of NBR was accompanied by an increase in gel content of the rubber due to the cross-linking side reaction. After reaction, the rubber was not completely soluble in any organic solvent. The extent of gelation greatly affects the physical properties of the product and highly gelled products are difficult to process. Therefore, the gel content of the HNBR product is monitored by measuring its relative viscosity or absolute molecular weight. In addition, several methods were used to control the cross-linking side reaction. This includes finding suitable system compositions and operational conditions to minimize the cross-linking, finding catalysts that may break cross-linking in the product. Further understanding of the mechanism of cross-linking may be achieved from such experiments.

3.4 Experimental Methods

General information about the chemicals, investigation methods, experimental procedures and operation procedures for characterization used for the research work are described in this chapter.

3.4.1 Materials

3.4.1.1 Commercial acrylonitrile-butadiene-rubber (NBR) latex

The commercial NBR latex (Perbunan 3431F, with a solid content of 19.5 wt.%) was provided by Lanxess Deutschland GmbH. The NBR contains 34 mol.% acrylonitrile and had a Mn = 70,000 (±2%) g/mol with a poly-dispersity index (PDI) of 3. Bases on previous experimental results regarding the latex stability in hydrogenation[76], diluted commercial NBR latex (solid NBR polymer content of 5 wt.%) was used in the experiments if not specified.

3.4.1.2 Reaction gas used in NBR latex hydrogenation

Oxygen free hydrogen gas (99.99%), ultra high purity nitrogen gas (99.999%) and propylene gas (99.0%) used in the reactions were provided by Praxair Inc (Kitchener, Canada).

3.4.1.3 Catalysts and solid chemicals for NBR latex hydrogenation

Rhodium chloride hydrate ($RhCl_3{\cdot}xH_2O$, Rh 38~40 wt.%), reagent grade fuming sulfuric acid (H_2SO_4, 30 wt.% free SO_3,) and triphenylphosphine (PPh_3, 99 wt.%) were purchased from Sigma-Aldrich (Canada) and used as received.

Wilkinson's catalyst, $RhCl(PPh_3)_3$, was received from Lanxess Deutschland GmbH. The water soluble analogues of the Wilkinson's catalyst, $RhCl(TPPMS)_3$ and $RhCl(TPPTS)_3$ were prepared by reacting $RhCl_3$ with the corresponding ligand in ethanol [77, 78]. The monosulfonated triphenylphosphine (TPPMS) ligand was synthesized in the lab while the trisulfonated triphenylphosphine (TPPTS) ligand was purchased from Sigma-Aldrich. The Grubbs second generation catalyst (G2) and Hoverda-Grubbs second generation catalyst (HG2) were purchased from Sigma-Aldrich.

3.4.1.4 Solvents and liquid chemicals for NBR latex hydrogenation

Reagent grade monochlorobenzene (MCB), methyl ethyl ketone (MEK) and acetone were all purchased from Fisher Scientific (Canada). Reagent grade acrylonitrile (AN), alcohols (e.g. methanol, ethanol and 2-propanol) and 1-hexene were obtained from Sigma-Aldrich (Canada). Deionized water was received from chemistry store (University of Waterloo). All these solvents were used as received. Gel permeation chromatography (GPC) grade tetrahydrofuran (THF) was purchased from Honeywell (USA) and was filtered before it was used for GPC analysis.

All of the chemicals specifically used for synthesizing in house NBR latex are summarized in the corresponding section.

3.4.1.5 Materials for synthesis of in-house NBR latex via emulsion copolymerization

Reagent grade acrylonitrile (99%), potassium persulfate, tert-dodecyl mercaptan (mixture of isomers, 98.5%) hydroxylamine solution (50 wt.% in H_2O) and technical grade sodium oleate (83 wt.%) were received from Sigma-Aldrich. Technical grade 1, 3-butadiene (99%) was obtained from Air Liquide (Canada).

3.4.2 NBR latex hydrogenation procedures

Hydrogenation reactions were conducted in a stirred, 300 mL autoclave (Parr Instrument, USA), which was cleaned by washing thoroughly with acetone and drying in a vacuum oven for 15 minutes after each reaction. The reaction temperature was monitored using a thermocouple. A dip tube placing inside the reactor was connected to the liquid sampling outlet. The catalyst addition device was installed in the head of the reactor. Specific experimental processes under different catalysts are described in the corresponding chapters.

3.4.3 Synthesis of NBR latex via emulsion copolymerization of acrylonitrile and butadiene

NBR latex was synthesized via an emulsion copolymerization method [79]. The polymerization reaction was performed in a 300 mL Parr autoclave. The reactor chilled in ice-water bath was charged with distill water, acrylonitrile (monomer), sodium oleate, tert-dodecyl mercaptan and potassium persulfate. After assembling the reactor, the mixture was degassed and purged with nitrogen gas for 30 minutes. Then liquefied 1, 3-budadiene (monomer) was quickly added and copolymerized with acrylonitrile at 30 ℃ using an emulsion polymerization procedure. After reaching a desired conversion, hydroxylamine was added to terminate polymerization. The residual portions of acrylonitrile and 1, 3-butadiene were eliminated by steam distillation at 70 ℃.

3.4.3.1 Overall NBR Polymerization Conversion

A gravimetric method was used to investigate the overall polymerization conversion. The monomer conversion (Conv. %) is defined as follows:

$$\mathbf{Conv.\ \% = W_{polymer} / W_{total} \times 100\ \%}$$

where $W_{polymer}$ and W_{total} represent the polymer in the reactor and the total monomer in the recipe, respectively.

3.4.3.2 Solid Content of the NBR latex

The solid content is defined as the mass of polymer (NBR) per volume of latex (g/L). To determine the solid content in the NBR latex, a small amount of latex (10 mL) was measured using a volumetric pipette. Sufficient Ethanol and NaCl solution (10 wt.%) was added drop by drop to the latex with stirring. The precipitated NBR was filtered using a Buchner funnel and washed with water to remove the surfactant and subsequently dried in a vacuum oven before being weighed.

3.4.4 Characterization

3.4.4.1 Determination of hydrogenation conversion

The conversion of NBR was obtained via Fourier-transform infrared (FT-IR) analysis using a Bio-Rad FTS 3000MX spectrometer or ^{1}H N.M.R.

To prepare the HNBR sample for FT-IR, the HNBR isolated from the latex was dissolved in methyl ethyl ketone 5% (wt./vol.). The polymer solution was cast onto a single NaCl crystal disc and dried to form a thin polymer film (< 1 mm). The degree of hydrogenation was calculated from the FT-IR spectra according to the peak strength [80]. However, it has been found FT-IR shows inconsistent results on HNBR at very low conversion (less than 20 mol.%). Therefore, the degree of hydrogenation of these samples was further verified by ^{1}H NMR.

^{1}H NMR spectra were recorded on a Bruker 300 MHz Spectrometer (Bruker BioSpin Corp. Massachusetts, USA) and chemical shifts were reported in ppm units with TMS as an internal standard. The sample solutions were prepared by dissolving dried polymer solid into $CDCl_3$.

3.4.4.2 Determination of metal concentration in HNBR via polymer digestion and ICP-OES

HNBR samples were digested by an improvement to the literature method [81]: 400~500 mg of HNBR polymer solid was accurately weighed out and mixed with hydrochloric acid (1 mL, 37.5 vol.%), nitric acid (5 mL, 62 vol.%) and aqueous hydrogen peroxide (1mL 30 vol.%). The sample was then digested in a High Pressure Asher (Anton Parr, Austria), under a high "organic program" (program condition, 300 ℃, and 130 bar for 3 hours). The metal concentration was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, TELEDYNE, LEEMAN Labs, Prodigy, high dispersion ICP, USA) [82]. Commercial rhodium solution (1000 mg/L Rh in HCl, Sigma-Aldrich) and ruthenium solution (10000 μg/mL Ru in 7 wt.% HCl, Sigma-Aldrich) were used as standard references for ICP calibration.

3.4.4.3 Measurement of viscosity of NBR and HNBR

To assess the solution viscosity of a given polymer, 0.25 g HNBR was weighed and transferred to a 25 mL volumetric flask which contains methyl ethyl ketone (MEK) and mixed thoroughly. The solution was then transferred to an Ubbelohde capillary viscometer through a disc filter (0.4 μm). Experimental data consisted of two measurements of the time required for the constant volume of solution to drain through the viscometer capillary. All viscosity measurements were carried out at 35 ℃ and reported as the elution time of the sample relative to that of pure methyl ethyl ketone at this temperature.

3.4.4.4 Molecular Weight and its Distribution

The average molecular weights (MW) and the molecular weight distribution (PDI) of the NBR and HNBR were determined by gel permeation chromatography (GPC, Wyatt Technology Corporation, California, USA) equipped with an RI detector (Waters 150-CV refractive index detector) and a multi-angle laser light scattering (DAWN® DSP-F Laser Photometer). The dried NBR/HNBR samples were dissolved in THF and filtered through a 45 mm syringe filter with 250 nm GHP membrane (Pall Corporation, New York, USA) and then 100 μL of the solution was injected into the GPC system using THF as eluent at a flow rate of 1.0 mL/minute at 30 ℃. A polystyrene standard (Mn = 96,722 g/mol and Mw = 98,251 g/mol) was used for checking.

3.4.4.5 Particle size and particle size distribution

The size and number size distribution (non-negative least squares method) of the polymer particles of the synthesized latex were determined by dynamic light scattering (DLS) at 25 ℃ using a Nanotrac 150 particle size analyzer (BETATEK Inc. Toronto, CA) and reported as the number average diameter. The calculations of the particle size distributions were performed using Microtrac FLEX 10.2.14 software available from BETATEK Inc., which employed single-exponential fitting, non-negatively constrained least-squares (NNLS), cumulants analysis, and CONTIN particle size distribution analysis routines.

3.4.4.6 Transmission electron microscopy (TEM) analysis

LEO 912 AB 100KV Energy Filtered Transmission Electron Microscopy (EFTEM) (Carl Zeiss Inc. Germany) was used to confirm the size and observe the morphology of the NBR particles. When preparing the NBR samples for TEM measurement, the commercial latex was firstly diluted with distilled water and then 10 μL of the diluted solution was incubated on a 400-mesh copper grid at room temperature. Excess solution was drawn off the edge of the grid with tissue paper. Next the grid was negatively stained with 2% (wt./vol.) uranyl acetate for 1 minute. After the excess stains were drawn off with tissue paper, the grid was delivered into the TEM chamber for imaging.

3.4.4.7 UV-Vis analysis

The solubility of HG2 catalyst is measured by UV-vis spectroscopy (Bio UV 3000, Varian, USA). A capped UV cell (3 mL) was used in this investigation. For the catalyst in organic solution, different concentrations of HG2 catalyst or G2 catalyst in CH_2Cl_2 solution were prepared in the UV cell in a nitrogen glove box and then measured by UV-vis. For the catalyst in aqueous water, about 0.005 g HG2 catalyst or G2 catalyst were added into a UV cell and mixed with 2.5 mL of water containing surfactant (ca. 1 g). The cell was hand-shaken and the optical density of the resulting solution was measured.

Chapter 4

NBR latex hydrogenation by in-situ synthesized $RhCl(PPh_3)_3$ catalyst

4.1 Introduction

It has been reported that NBR latex could be hydrogenated using $RhCl(PPh_3)_3$ in the presence of an excess of triphenylphosphine (PPh_3) [45]. The transportation of the $RhCl(PPh_3)_3$ catalyst into the latex particles was facilitated by the PPh_3. However, the NBR hydrogenation reaction using $RhCl(PPh_3)_3$ catalyst in latex was much slower than that in homogeneous NBR solution [10]. Different from in polymer solution where hydrogenation reaction was carried out at a molecular level, the contact between the catalyst and NBR is substantially limited in the aqueous latex. Thus, improving the dispersion of the catalyst in the aqueous system became a major issue.

As we know, $RhCl_3$ is highly water soluble and commonly utilized as the rhodium catalyst precursor for synthesizing different types of rhodium complexes [83, 84]. Therefore, direct in-situ synthesis of $RhCl(PPh_3)_3$ from $RhCl_3$ and PPh_3 in the NBR latex was developed and investigated on NBR latex hydrogenation. The results are compared with those obtained with the pre-made solid $RhCl(PPh_3)_3$ catalyst.

4.2 Experimental

4.2.1 In-situ synthesis of $RhCl(PPh_3)_3$ from $RhCl_3$ and PPh_3 in water

A certain amount of $RhCl_3$ and PPh_3 (1: 3 mol./mol.) was added to the water under a N_2 atmosphere in the flask. Then the flask was heated to 100 ℃ for several minutes and cooled down to room temperature. The resultant solid precipitate was filtered, washed with water and dried under vacuum.

4.2.2 Hydrogenation of NBR Latex via in-situ synthesized $RhCl(PPh_3)_3$ catalyst

Similar to the NBR latex hydrogenation using pre-made solid $RhCl(PPh_3)_3$, the hydrogenation reaction with in-situ $RhCl(PPh_3)_3$ was conducted in a 300 mL Parr reactor. The catalyst precursor $RhCl_3$ was placed in a catalyst addition device (Parr Instrument, USA) installed in the head of the reactor. PPh_3 was mixed with the NBR latex. Total volume of the NBR latex is 100 mL. The NBR-PPh_3 mixture was degassed and heated to the reaction temperature. Subsequently, the catalyst precursor was charged to the mixture together with hydrogen gas. The hydrogen pressure and reaction temperature were kept constant throughout the reaction. The reaction mixture was sampled at intervals during the reaction.

4.2.3 Characterization

The conversion of the NBR to HNBR was measured by both FT-IR and ^1H NMR. The relative viscosity of NBR and the resultant HNBRs were measured by Ubbelohde capillary viscometer. The residual metal concentration in polymer particles was measured by ICP-OES. The morphology of the NBR latex was measured by DLS and TEM. Detailed characterization procedures have already been provided in Chapter 3.

4.3 Results and discussion

4.3.1 In-situ synthesis of $RhCl(PPh_3)_3$ in aqueous system

Generally, the standard procedure of synthesizing $RhCl(PPh_3)_3$ is from $RhCl_3$ and PPh_3 in ethanol [85]. We first investigated the in-situ synthesis of $RhCl(PPh_3)_3$ in aqueous system.

In the in-situ synthesis experiment, it was found that solid PPh_3 liquefied around 80 ℃. After adding $RhCl_3$, the color of PPh_3 droplets quickly changed from transparent to yellow. When reactor was cooled down to room temperature, these yellow droplets solidified and precipitated. Figure 4-1 shows the FT-IR spectral of $RhCl(PPh_3)_3$ (a), pure PPh_3 (b) and the precipitate (c) respectively. From the FT-IR results, although the spectrum of precipitate is similar to that of PPh_3, the distinctive peak at 550 cm^{-1} attributed to a Rh-P stretching vibration was observed [86, 87], showing the existence of $RhCl(PPh_3)_3$. The color change of PPh_3 also indicated the formation of $RhCl(PPh)_3$. Since $RhCl(PPh_3)_3$ is insoluble in water, it is prone to reside in the PPh_3 droplet which is also hydrophobic. After carefully washing with hot ethanol, most of the precipitates were re-dissolved in ethanol (PPh_3 is soluble in hot ethanol). The final residue solid was analyzed by FT-IR spectroscopy which showed the same spectrum to $RhCl(PPh_3)_3$.

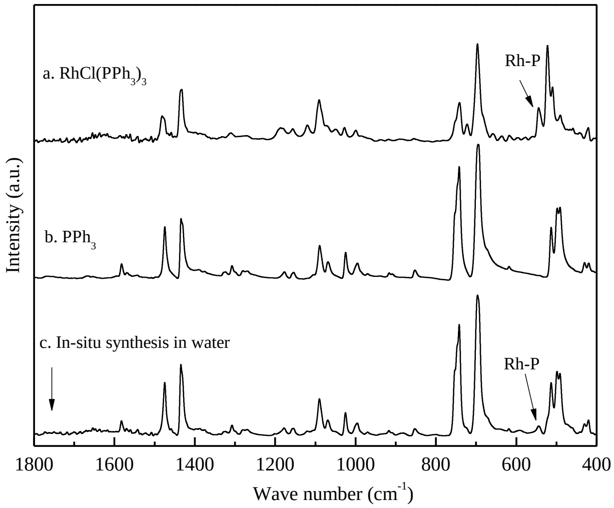


Figure 4-1 FT-IR spectra of different solid materials (a) $RhCl(PPh_3)_3$, (b) PPh_3, (c) in-situ synthesis of $RhCl(PPh_3)_3$ in water

Reaction condition for (c): 100 mL H_2O, T = 145 ℃, t = 15 min, $RhCl_3$ = 0.052 mmol, 1.8 mmol PPh_3

In addition, the in-situ synthesized $RhCl(PPh_3)_3$ was further dried and weighed. The yield was calculated based on the feed $RhCl_3$ using the following Equation. It was found that less than 20 mol.% of rhodium from feed $RhCl_3$ was converted to $RhCl(PPh_3)_3$ in water.

$$\textbf{Yield (mol.\%)= Rh}_{\textbf{(in Wilkinson's catalyst)}} \textbf{ / Rh}_{\textbf{(in feed RhCl3)}}$$

4.3.2 NBR latex hydrogenation using in-situ synthesized $RhCl(PPh_3)_3$

Table 4-1 NBR latex hydrogenation by different rhodium complex

Entry	Catalyst/Precursor mmol/L		PPh_3 mmol/L	$^*PPh_3/Rh$ molar ratio	Temperature ℃	Time h	Conversion mol.%
1	$RhCl(PPh_3)_3$	0.52	18	35	145	50	95
2		0.52	18	35	160	26	95
3		0.52	0	0	145	50	<20
4	$RhCl_3.xH_2O$	0.52	0	-	145	50	0
5		0	18	-	145	50	0
6		0.52	18	35	145	38	95
7		0.52	18	35	160	19	95
8		0.52	18	35	160	20	96

NBR latex: 50 g/L, total volume = 100 mL, P_{H_2} = 1000 psig, [Rh]/[C=C] = 1080 (mol./mol.)

*Added PPh_3. Not includes the amount of PPh_3 in $RhCl(PPh_3)_3$ catalyst

Representative experiments under operational conditions and final conversions of NBR latex hydrogenation using pre-made solid $RhCl(PPh_3)_3$ catalyst and in-situ synthesized $RhCl(PPh_3)_3$ catalyst are listed in Table 4-1. Two temperatures 145℃ and 160℃ were used in the investigations. First, it can be seen that NBR latex could successfully be hydrogenated under pre-made solid $RhCl(PPh_3)_3$ together with PPh_3 (Entry 1, 2). Without adding PPh_3, the hydrogenation reaction was slow and only part of C=Cs was reacted (Entry 3). In the in-situ method, $RhCl_3$ could not catalyze the hydrogenation reaction (Entry 4). After adding PPh_3, it was found that the

C=Cs in NBR could be quantitatively hydrogenated, indicating that $RhCl(PPh_3)_3$ was in-situ synthesized in the NBR latex from $RhCl_3$ and PPh_3.

Under identical reaction conditions, it is clearly seen that NBR hydrogenation reaction was faster using the in-situ synthesized $RhCl(PPh_3)_3$ catalyst than the pre-made solid counterpart. The hydrogenation reaction time (both hydrogenated to 95 mol.%) was shortened from 50 hours to 38 hours at 145 ℃ (Entry 1 vs. Entry 6) and from 26 hours to 19 hours at 160 ℃ (Entry 2 vs. Entry 7). In addition, the reproducibility of this reaction was also tested and a satisfactory result was observed (Entry 7, 8).

4.3.3 Hydrogenation characterization

4.3.3.1 FT-IR analysis

Typical FT-IR spectra of original NBR (a), hydrogenated NBR (b) obtained using in-situ $RhCl(PPh_3)_3$ are depicted in Figure 4-2. In the spectrum of NBR, the peak at 2236 cm^{-1} belongs to the -CN stretching vibration. The intense peak shown at 970 cm^{-1} is the characteristic of the level of olefin by the carbon- hydrogen vibration of the 1, 4-trans double bonds. The absorbance at the peak of 920 cm^{-1} is the 1, 2 vinyl terminal bonds. The absorption band at 714 cm^{-1} corresponding to the 1, 4-cis structural units was not observed for the preliminary NBR sample.

After hydrogenation, it was observed that the intensity of peaks at 970 cm^{-1} and 920 cm^{-1} considerably diminished while a peak at 723 cm^{-1} appeared. The peak at 723 cm^{-1} in the hydrogenation NBR corresponds to the saturated $-[CH_2]_n-$ unit (n>4). This transformation indicates the reduction of unsaturated C=C bonds to saturated C-C bonds. The chemical stability of unsaturated nitrile group during the hydrogenation was also measured. Both the presence of nitrile group in HNBR and the lack of primary (two bands from 3250 cm^{-1} to 3400 cm^{-1}) or secondary amines (one band from 3310 cm^{-1} to 3350 cm^{-1}) confirms that the hydrogen reduction is exclusively towards C=C bonds. In addition, a new peak at 2214 cm^{-1} was observed in HNBR (Figure 4-3) which is attributed to the positional isomerization of C=Cs bonds [88]. Since no positional isomerization was observed using the pre-made solid $RhCl(PPh_3)_3$ catalyst, this positional isomerization is very likely triggered by the catalyst precursor $RhCl_3$.

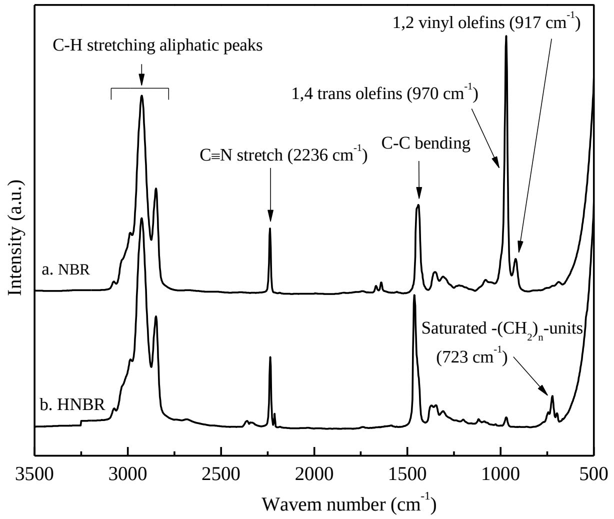


Figure 4-2 Typical FT-IR spectra of NBR and hydrogenated NBR

(a) NBR before hydrogenation, (b) hydrogenated NBR (95 mol.%), NBR latex = 50 g/L, $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig)

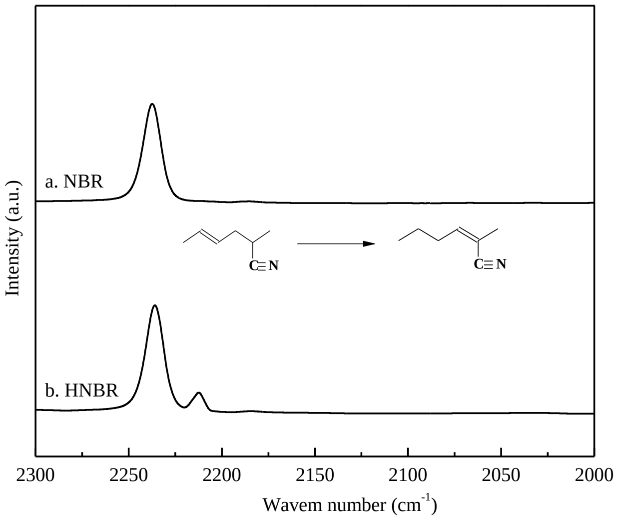


Figure 4-3 FT-IR evidence of C=C double bond migration in NBR hydrogenation

(a) NBR before hydrogenation, (b) hydrogenated NBR (95 mol.%, NBR latex = 50 g/L, $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig)

4.3.3.2 ^{1}H NMR analysis

Figure 4-4 shows the chemical shifts of the protons in NBR and hydrogenated NBR by ^{1}H NMR characterization. For NBR, the peaks from 5.6 to 4.9 ppm are attributed to the olefinic protons. Among them, the large peaks between 5.3 and 5.6 ppm are related to trans hydrogen atoms of butadiene resulting from 1,4-addition and the small peaks between 4.91 and 5.1 ppm belong to the hydrogen atoms of pendant vinyl groups which comes from 1,2-addition. Meanwhile, all of the aliphatic protons in the CH_3, CH_2 and CH microstructures lie between 0.8 and 2.8 ppm. In the HNBR (95 mol.%), it could be clearly seen that most of the peaks in the olefinic protons region disappeared which confirms the unsaturated C=Cs were reduced by H_2.

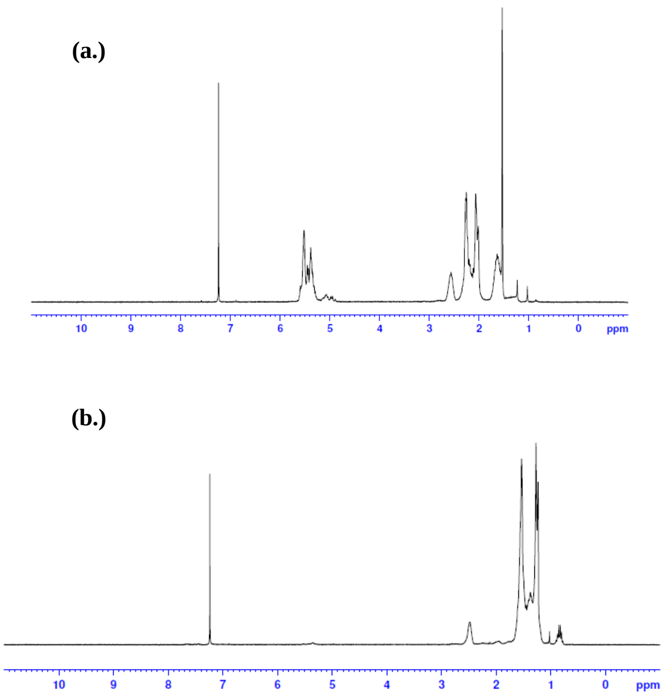


Figure 4-4 Typical ^{1}H NMR spectra of NBR and hydrogenated NBR

(a.) NBR, (b.) HNBR (95 mol.%, NBR latex = 50 g/L, $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig)

4.3.4 Characterization of the NBR/HNBR during hydrogenation

4.3.4.1 The particles size of NBR in NBR latex

We next turn our attention to the morphology of the latex. Dynamic light scattering (DLS) experiments showed that during the hydrogenation operations, no coagulation of the latex was observed under our reaction conditions. The average particle size of the NBR latex is around 72 nm. It remained the same after the hydrogenation reaction (Figure 4-5). The solid content of the resultant HNBR latex is also compared to NBR latex. The difference is less than 5 wt.% in average. All these results showed that NBR hydrogenation using in-situ synthesized $RhCl(PPh_3)_3$ catalyst wouldn’t affect latex particle size or stability.

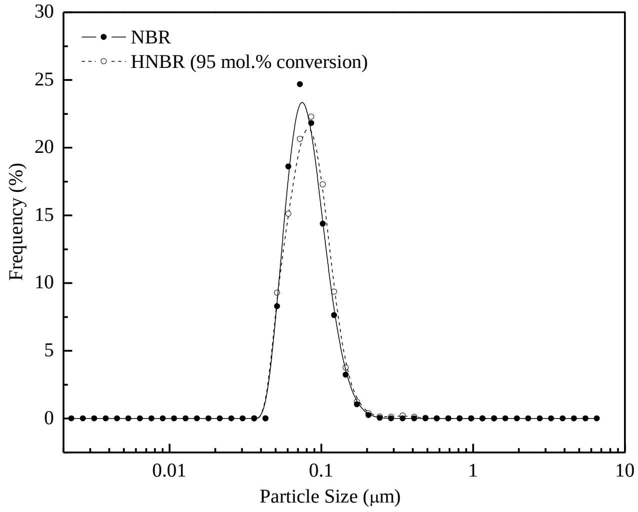


Figure 4-5 Particle size distributions in the lattices before/after hydrogenation

NBR latex = 50 g/L, $RhCl_3^{\cdot}$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig

Figure 4-6 shows TEM micrographs of NBR latex before/after the hydrogenation step. Since the staining agent can only stain double bonds, lightly colored domains should indicate lower double-bond concentrations. For comparison, NBR latex (A) and the HNBR latex with a 95 mol.% conversion (B) are also depicted. The non-hydrogenated NBR (A) shows relatively dark because the concentration of the staining agent inside the particle is high. On the other hand, the hydrogenated HNBR latex (B) exhibits a much lighter color due to the low level of double bonds available for staining.

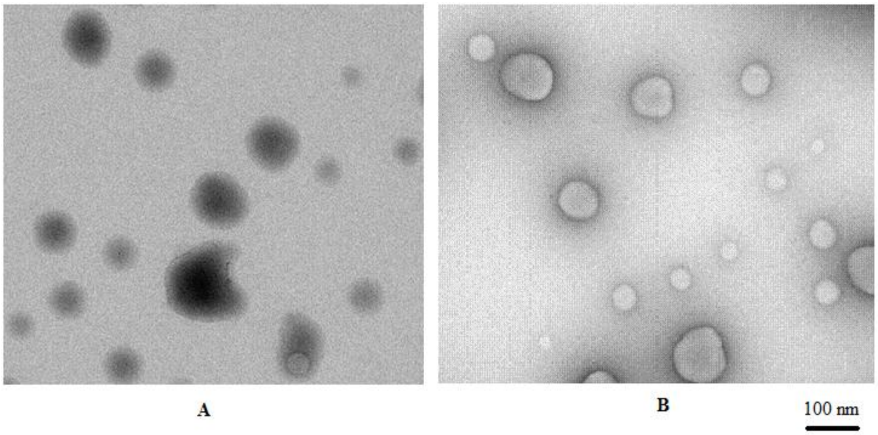


Figure 4-6 TEM micrographs of (A) NBR latex; (B) HNBR latex

HNBR (95 mol.% conversion), NBR latex = 50 g/L, $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig

4.3.4.2 The viscosity of the NBR/HNBR

The changes in polymer chemistry structure such as degradation (the reduction of molecular weight process) and cross-linking (the increase of molecular weight process) during the reaction are very important since they have great impact on the physical properties (e.g. viscosity) of the HNBR product. The severe cross-linking reaction could give rise to the gel formation which greatly affects HNBR processibility in manufacturing.

To quickly detect whether any gel in the resultant HNBR, the synthesized HNBR was precipitated from the latex and then re-dissolved in mono-chlorobenzene (MCB). It was found that the HNBR from using solid $RhCl(PPh_3)_3$ could be quickly dissolved in MCB while the HNBR made from in-situ process swelled in the solvent first and slowly dissolved over night. Although no visible gel was observed in the in-situ method, the dissolving process indicated that a small amount of gel probably might be existed in the HNBR product. As the cross-linking reaction occurred with the coagulated single NBR particles, the extension of gel formation should be limited.

As gel formed, the viscosity of the HNBR solution will change. Therefore, this change could be used to reflect the extension of gel formation. The viscosity of HNBR in methyl ethyl ketone (MEK) to pure MEK solvent was used to measure the relative viscosity of the HNBR. From Table 4-2, it can be seen that HNBRs obtained from using solid catalyst showed a similar relative viscosities under different reaction system. This showed the cross-linking reaction is irreverent to the reaction media. When using the in-situ synthesized catalyst, the resultant HNBR possessed large value in relative viscosity. This result is in agreement with the previous dissolution results, showing the occurrence of cross-linking side reaction during the hydrogenation.

Table 4-2 Viscosity results for HNBR made by different catalytic systems

Sample	Catalytic system	Reaction media	Relative Viscosity ($\eta_{rel.}$*)
HNBR[1]	Solid $RhCl(PPh_3)_3$	solution	3.65
HNBR[2]	Solid $RhCl(PPh_3)_3$	latex	3.72
HNBR[3]	in-situ process, $RhCl_3 + PPh_3$	latex	4.72

[1] HNBR from NBR solution hydrogenation (95 mol.% conversion)

[2] NBR latex = 50 g/L, $RhCl(PPh_3)_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig, conversion = 95 mol.%

[3] NBR latex = 50 g/L, $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig, conversion = 95 mol.%

Since the in-situ synthesized $RhCl(PPh_3)_3$ is not responsible for the extended increase in the relative viscosity, the cross-linking reaction is probably caused by the catalyst precursor $RhCl_3$. Although we could not find direct evidence, we observed the same C=C migration from FT-IR spectrum as Parent et al. studied NBR solution hydrogenation using $OsHCl(CO)(O_2)(PCy_3)_2$ catalyst where they claimed the migration was related with the cross-linking reaction [89].

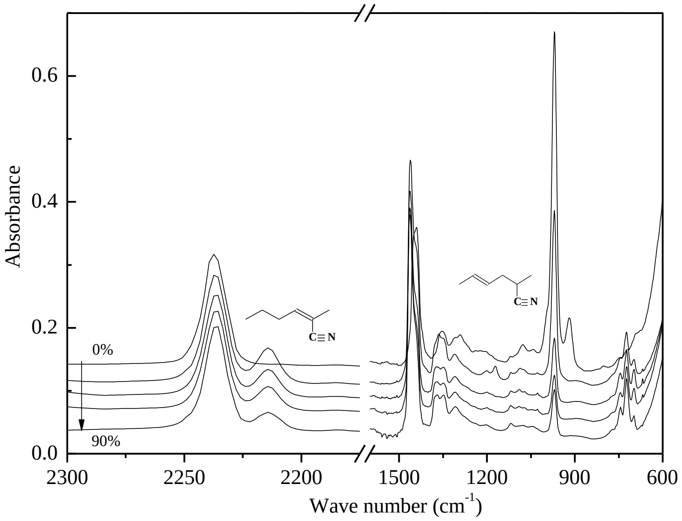


Figure 4-7 The course of olefin migration during latex NBR hydrogenation under in-situ process

NBR latex = 50 g/L, $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig

Figure 4-7 illustrates the development of migration over the course of hydrogenation. It can be seen that this double bond migration occurred quickly at the beginning of the NBR hydrogenation reaction. This activated olefin, by nature of its adjacent nitrile group, would be relatively electron deficient and therefore less susceptible to be hydrogenated. However, while the other C=C bonds were reduced, this conjugated C=C proportion remained almost constant during the hydrogenation. This is probably due to the fact that in-situ formed $RhCl(PPh_3)_3$ could not reach such C=Cs for hydrogenation due to a steric hindrance in the latex system since the polymer chains in particle are coiled. To verify it, a partially hydrogenated NBR (30 mol.% conversion) from in-situ method was precipitated, dried and re-dissolved in mono-chlorobenzene for hydrogenation using the same catalyst. It was found that all of the C=C bonds could be hydrogenated. Therefore, we can conclude the cross-linking reaction is related to a reaction promoted by the catalyst precursor $RhCl_3$.

4.3.5 The diffusion of the catalyst in NBR latex hydrogenation

The hydrogenation of high molecular weight polymeric materials in latex is quite different from the hydrogenation of small molecules in aqueous/organic biphasic system. The polymer hydrogenation reactions were normally conducted at a temperature between glass transition temperatures (T_g) and melting temperature (T_m) of the polymer. Hence, 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 the polymer chains [90]. On this basis, the contact of C=C bonds with the catalyst should mainly depend on the diffusion of the catalyst through the particle. Meanwhile, due to the requirement for industrial applications of HNBR, partial hydrogenation of the C=C bonds (e.g. C=C bonds at the surface) in the polymer chains is insufficient. In order to do this, the catalyst needs to contact all of the C=C bonds to promote the hydrogenation reaction.

Generally, the catalyst can be presented in three locations in the polymer latex: i) in the water medium, ii) at the interface of water and polymer particles and iii) inside of the polymer particles. Parker and Roberts, who studied the hydrogenation of SBR latex, found that the hydrogenation reaction begins after the catalyst contacts the surface of the polymer particles [91]. From our results (Table 4-1, Entry 3), less than 20 mol.% C=Cs in NBR was reduced by the hydrophobic catalyst $RhCl(PPh_3)_3$ alone because the contact between the catalyst and C=Cs in the aqueous system is greatly limited. Therefore, in order to achieve the required degree of hydrogenation in

NBR latex, the catalyst must diffuse into the polymer particles. When an experiment for NBR latex hydrogenation using $RhCl(PPh_3)_3$ with the of the presence of additional PPh_3,more than 95 mol.% conversion was achieved (Table 4-1, Entry 1 and 2). Therefore, in NBR latex hydrogenation, the addition of extra PPh_3 is required. The additional PPh_3 acted as a reagent (carrier) to facilitate phase boundary crossing of the catalyst dissolved in it. From our FT-IR spectra (Figure 4-8 b), two characteristic peaks for PPh_3 [92] were observed when NBR latex was mixed with PPh_3 at elevated temperature, confirming PPh_3 could diffuse into the NBR polymer particles. Hence, PPh_3 is not only used as a ligand for in-situ synthesizing $RhCl(PPh_3)_3$ but also works as a carrier for catalyst transportation during the NBR latex hydrogenation.

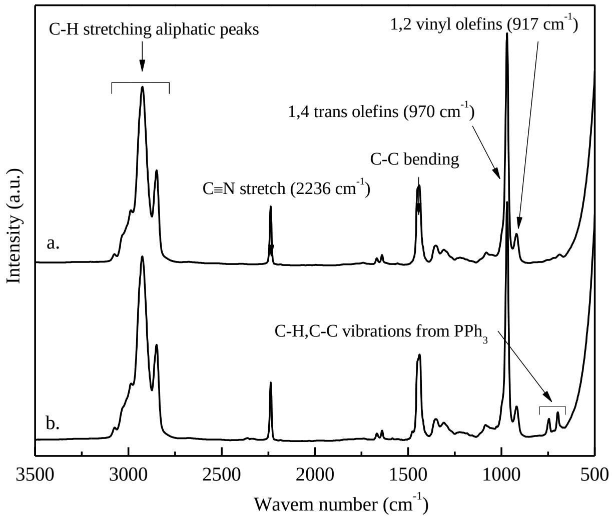


Figure 4-8 Transportation of PPh_3 from the aqueous phase to NBR particles in NBR latex

(a) NBR, (b) NBR from NBR latex with PPh_3 at elevated temperature (50 g/L NBR latex, PPh_3 = 18 mmol/L, T = 145 ℃)

To quantify the amount of catalyst resided in the polymer particles, the resultant HNBRs were digested and residual rhodium metal was measured by ICP-AES. Figure 4-9 shows the rhodium concentration in the polymer particles during the hydrogenation. When using the pre-made solid $RhCl(PPh_3)_3$ catalyst, the catalyst diffusion was slow. The Rh concentration in the polymer particles slowly increased and reached steady state (18 wt.%) after 15 hours. This is because when the hydrophobic catalyst $RhCl(PPh_3)_3$ was added to the NBR latex, it cannot well disperse into the aqueous phase. Instead, it remained as suspended clusters in the water phase or settled down. In the presence of extra PPh_3 under reaction temperature, $RhCl(PPh_3)_3$ was dissolved in PPh_3 droplets and transferred into the NBR particles with the help of PPh_3. Hence, $RhCl(PPh_3)_3$ catalyst needs to cross the two interfaces (the catalyst-water interface and water-micelles interface) before contacting the C=C bonds in NBR particles.

In the in-situ process, the catalyst precursor $RhCl_3$ could be well dissolved in the aqueous NBR latex. It could easily react with PPh_3 droplets, forming $RhCl(PPh_3)_3$ catalst. The in-situ synthesized catalyst was dissolved in PPh_3 droplets and diffused into the polymer particles. Thereby, the rhodium concentration in the particles increased rapidly and the steady state reached in a short time. Comparing with using solid catalyst, the retention of catalyst inside the polymer particles was slightly higher using the in-situ method. The quick catalyst diffusion and the high catalyst retention caused a faster hydrogenation reaction in the in-situ process.

Comparing the molar percentage of rhodium in the polymer to the total feed rhodium from $RhCl_3$, it was found that less than half of the total rhodium were transferred into the polymer particles using the in-situ method. This could be explained by the low in-situ synthesis efficiency in the NBR latex system. In addition, and a layer of black particles (Rh colloid) was also observed at the bottom of the reactor after reaction. This is resulted by the reduction of $RhCl_3$ to a metallic Rh at high temperature under H_2. A similar phenomenon was observed by G. Papadogianakis et al. in hydrogenation of polybutadiene-1, 4-block-poly(ethylene oxide) latex using in-situ synthesized Rh/TPPTS catalyst [93]. Meanwhile, the activity of the metallic Rh was tested for NBR latex hydrogenation before and no hydrogenation was observed [76].

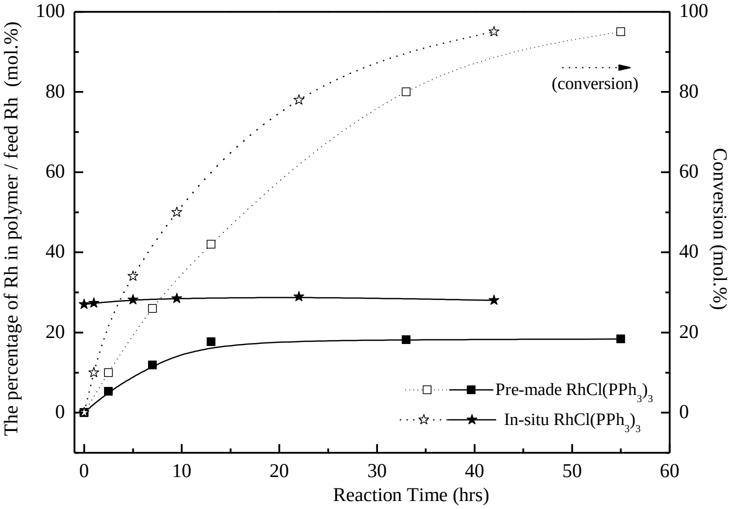


Figure 4-9 The change of rhodium concentration in NBR polymer particles through hydrogenation

Dash line, hydrogenation conversion (mol.%); solid line, rhodium in polymer/total rhodium feed (mol.%),

NBR latex = 50 g/L, $RhCl_3$ or $RhCl(PPh_3)_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig

4.3.6 The effects of temperature, catalyst loading and PPh_3 on the $RhCl_3$ ratio for NBR latex hydrogenation using the in-situ process

The effect of reaction temperature, PPh_3 to $RhCl_3$ ratio and catalyst precursor $RhCl_3$ loading are three important factors which have commonly been analyzed in NBR solution hydrogenation [94, 95]. Here, these factors on the extent of hydrogenation conversion were also studied for NBR latex hydrogenation and the results are summarized in Table 4-3. The NBR latex hydrogenation reaction under in-situ process was studied from 50 ℃ to 160 ℃ and at a constant reaction pressure and catalyst loading of 1000 psig and 0.52 mmol/L of $RhCl_3$ (Table 4-3, Entry 1-4 and Entry 8). It is clear that temperature is an important parameter on the hydrogenation reaction. The reaction temperature greatly affected the in-situ synthesis and catalyst diffusion efficiency. The hydrogenation reaction time (under same conversion) dropped with an increase in temperature. In addition, the rhodium metal concentration in the polymer product increased with an increase in temperature.

Table 4-3 NBR latex hydrogenation under in-situ process

Entry	**$RhCl_3 \cdot xH_2O$** mmol/L	**$*PPh_3$** mmol/L	**PPh_3/Rh** (mol/mol)	**T.** ℃	**Time** hrs	**Conv.** mol.%	$\frac{Rh_{polymer}}{Rh_{total}}$
1	0.52	18	35	50	100	<10	0.01
2	0.52	18	35	90	100	54	0.08
3	0.52	18	35	130	130	95	0.16
4	0.52	18	35	145	38	95	0.26
5	0.26	9	35	145	100	96	0.14
6	0.52	1.6	3	160	82	95	0.10
7	0.52	7.8	15	160	29	95	0.20
8	0.52	18	35	160	19	95	0.26
9	0.52	52	100	160	18	95	0.31
10	0.52	18	35	160	20	96	0.26
11	1.04	36	34	160	15	95	0.34
12	1.80	61	34	160	13	95	0.37

NBR latex = 100 mL (50 g/L), P_{H_2} = 1000 psig

* Additional PPh_3. Not includes the amount of PPh_3 in $RhCl(PPh_3)_3$ catalyst

The ratio of PPh_3 to $RhCl_3$.aq was studied at 160 ℃ at a constant $RhCl_3$ loading (Rh/NBR) and H_2 pressure (Entry 6-9). It was suggested that the free PPh_3 performed as the required free co-catalyst ligand to keep the stability of the main catalyst $RhCl(PPh_3)_3$ during the NBR solution hydrogenation and the PPh_3 had a marginal effect on the activity of the $RhCl(PPh_3)_3$ catalyst [96]. However, it can be seen that the PPh_3 plays a very significant role in the NBR latex hydrogenation reaction. The reaction time greatly decreased from 82 hours to 19 hours on increasing the PPh_3 to $RhCl_3$.aq ratio from 3 to 35. However the reaction time almost keeps constant when the ratio increases to 100. Although a larger amount of catalyst could diffused into the polymer particles with the addition of more PPh_3, the excessive PPh_3 would slow down the formation of reactive intermediate $RhCl(PPh_3)_2$ by shifting the equilibrium of the $RhCl(PPh_3)_3$ dissociation [97]. Also, the effect of the $RhCl_3$ loading was compared under different temperatures. It can be seen the reaction time was significantly affected under lower $RhCl_3$ loading (Entry 4, 5) while this was not so evident at higher loadings (Entry 10-12).

4.4 Catalyst in-situ synthesis with alcohol in NBR latex hydrogenation

In light of this new information of cross-linking in NBR latex hydrogenation under the in-situ method, one of the choices is to improve the in-situ synthesis efficiency is to convert more catalyst precursor $RhCl_3$ into $RhCl(PPh_3)_3$. Right now, the standard reference work [85] is the most familiar method for synthesizing $RhCl(PPh_3)_3$ using $RhCl_3$. In this method, $RhCl_3$ reacts with excess PPh_3 in ethanol to form $RhCl(PPh_3)$. Unfortunately, $RhCl(PPh_3)_3$ could not be efficiently synthesized in water due to the low solubility of PPh_3 in pure water. However, it was recently discovered that when the catalyst was synthesized in a mixture of water and alcohol, the yield of the catalyst could be improved to a great extent compared with using pure water alone

[98]. On this basis, in order to generate in-situ catalyst in a larger amount, a small amount of alcohol was added in the reaction system.

$$RhCl_3 + H_2O + 4PPh_3 \xrightarrow{\text{Ethanol}} RhCl(PPh_3)_3 + PPh_3O + 2HCl$$

The results of NBR latex hydrogenation in the presence of ethanol are shown in Figure 4-10. Under the in-situ method, it was found the hydrogenation reaction rate increased considerably after the introduction of ethanol. The reaction time greatly decreased from 38 hours to 20 hours at 145 ℃ (Figure 4-10). Also, the rhodium concentration in the polymer particles was also measured by the ICP-OES and more Rh metal was measured inside the polymer particles. It should also be noted that ethanol could not dissolve the $RhCl(PPh_3)_3$ or NBR polymer in the latex. No distinctive promotion in the hydrogenation reaction was observed when using pre-made solid catalyst (Table 4-4). Therefore, more $RhCl(PPh_3)_3$ catalyst should be in-situ generated under the NBR latex/ethanol mixture.

Table 4-4 NBR latex hydrogenation by $RhCl(PPh_3)_3/PPh_3$ adding ethanol

No	Ethanol	Reaction Time hrs	Conversion mol.%
1	No	21	95.5
2	Yes	20	96.0

NBR latex = 50 g/L, total volume = 100 mL, T = 160 ℃, P_{H_2} = 1000 psig

Without ethanol: $RhCl(PPh_3)_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L

With ethanol: $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, ethanol/total = 1/10 (vol./vol.)

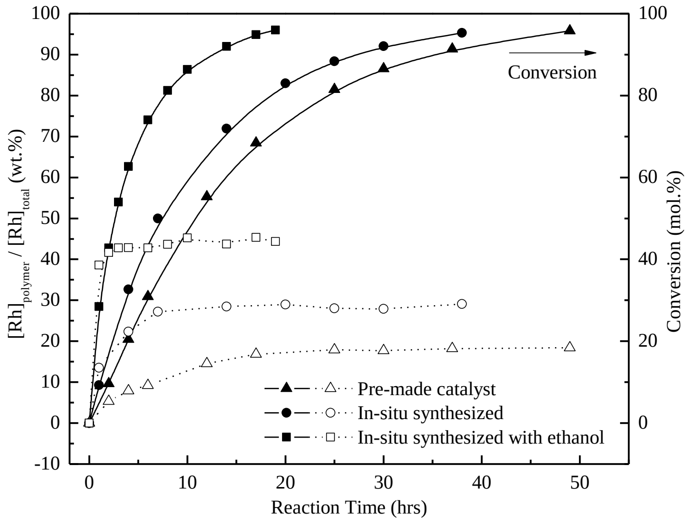


Figure 4-10 Hydrogenation conversion and rhodium concentration in NBR polymer particles under different catalytic systems

Solid line: hydrogenation conversion; dash line: rhodium in polymer/total rhodium,

NBR latex = 50 g/L, total volume = 100 mL, T = 145 ℃, P_{H_2} = 1000 psig

$RhCl(PPh_3)_3$ or $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L

In-situ with ethanol: $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, ethanol/total = 1/10 (vol./vol.)

The DLS results showed that after adding ethanol, the NBR particle size slightly increased from 72 nm to 80 nm. This is because when an alcohol diffused into the micelle, it can counter balance the charges and reduce the electrical repulsion in the stern layer of the micelles. In other words, the charge density at the micelles surface decreased and thereby the absolute value of the electrical potential was also reduced [99]. Similar results were reported by Li et al. when they added an alcohol in the 1-dodecene hydroformylation in a biphasic catalytic system [100].

The solubility of the HNBR product was also analyzed. The HNBR could be quickly dissolved in mono-chlorobenzene and no visible gel was observed. The relative viscosity results (Table 4-5) also showed that after introduction of a small amount of ethanol to the in-situ synthesis process the relative viscosity of the final HNBR reduced.

Table 4-5 The viscosity of HNBR from in-situ process

Sample	Catalytic system	Reaction media	Relative Viscosity (η_{rel}*)
HNBR[1]	in-situ $RhCl(PPh_3)_3$	Latex	4.22
HNBR[2]	in-situ $RhCl(PPh_3)_3$ with alcohol	Latex	3.92

NBR latex = 50 g/L, total volume = 100 mL, T = 145 ℃, P_{H_2} = 1000 psig

[1] $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L

[2] $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, ethanol/NBR latex = 1/10 (vol./vol.)

4.4.1 The effect of ethanol to NBR latex ratio

The effect of the ethanol to total volume ratio in the in-situ method is shown in Figure 4-11. It was found that the reaction became faster as the amount of ethanol volume ratio increased from 1/20 to 1/5, indicating most likely that more catalyst could be synthesized in-situ with higher levels of ethanol. However, it was also observed that further addition of ethanol to the diluted NBR latex interrupted the stability of latex. As a result, polymer particles were precipitated from the latex.

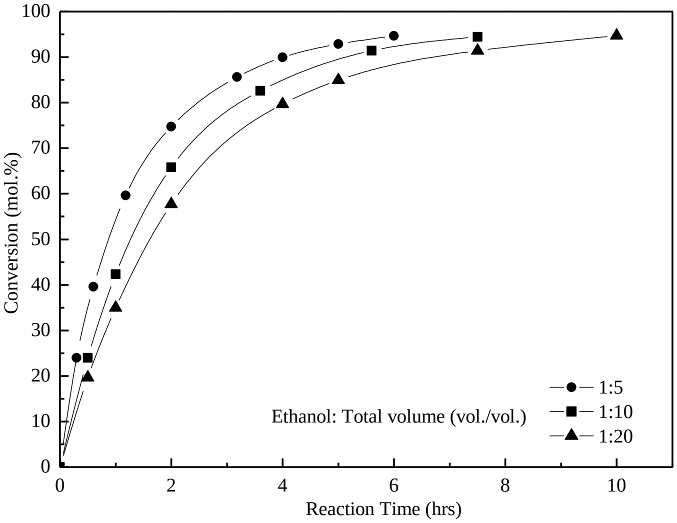


Figure 4-11 NBR latex hydrogenation with different NBR latex/ethanol volume ratio (in-situ process)

NBR latex = 50 g/L, $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, ethanol/total volume (vol./vol.): ● 1:5; ■ 1:10; ▲ 1:20, total volume = 100 mL, T = 160 ℃, P_{H_2} = 1000 psig

4.4.2 The effect of different kinds of alcohols

Attempts were also made to investigate the effect of different kinds of alcohols (same mol level) as additives for NBR latex hydrogenation (Figure 4-12). Under the same reaction condition, the reaction time decreased with the sequence of $t_{2\text{-propanol}} > t_{\text{ethanol}} > t_{\text{methanol}}$. For 2-propanol, due to its stronger reduction ability and lipophilic property (it can work as a surfactant), it more likely stays around the polymer particles and the in-situ formed catalyst can rapidly diffuse into the inside of the polymer particles. Therefore the hydrogenation reaction in the presence of 2-propanol is faster than that of ethanol or methanol.

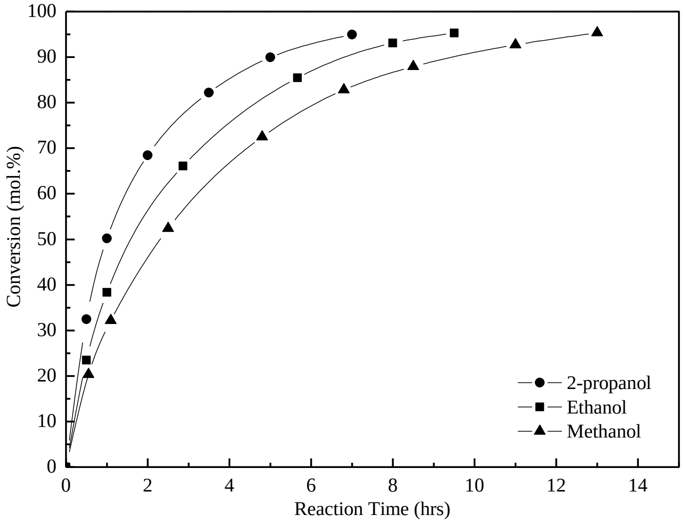


Figure 4-12 NBR latex hydrogenation with the addition of alcohol (in-situ process)

● 2-propanol; ■ ethanol; ▲ methanol, methanol: ethanol: 2-propanol = 1:1:1 (mol ratio), ethanol/total volume = 1/20 (vol./vol.)

NBR latex = 50 g/L, total volume = 100 mL, $RhCl_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 160 ℃, P_{H_2} = 1000 psig,

4.5 Conclusions

$RhCl(PPh_3)_3$ was in-situ synthesized in NBR latex from $RhCl_3$ and PPh_3 and used as a catalyst for hydrogenation of C=Cs in NBR. The key to this success is the fact that the hydrophilic catalyst precursor $RhCl_3$ is easily dispersed in water and the in-situ synthesized hydrophobic $RhCl(PPh_3)_3$ catalyst quickly diffused into the NBR swelled micelles. Compared with using pre-made solid $RhCl(PPh_3)_3$ catalyst, NBR latex hydrogenation reaction is faster using this in-situ method. The catalyst diffusion process was also investigated by monitoring the change of rhodium concentration in NBR particles. The result showed 1) high degree of hydrogenation can only be achieved when catalyst transported into the NBR particles in latex; 2) using the in-situ route, catalyst could be diffused into the polymer particles in a shorter time. In the in-situ method, the un-reacted $RhCl_3$ triggered an undesirable cross-linking reaction which was reflected by the change of relative viscosity of HNBR.

In addition, the in-situ method was further improved by mixing alcohol with the NBR latex under a suitable ratio. The catalytic system became more active since more $RhCl(PPh_3)_3$ catalyst was in-situ synthesized. As a result, the hydrogenation reaction was improved and the gel formation in HNBR products was reduced. This improvement is seen when using other alcohols.

Chapter 5

NBR latex hydrogenation with the water-soluble rhodium catalysts

We had discovered that $RhCl(PPh_3)_3/PPh_3$ is an effective catalytic system for hydrogenation of NBR in aqueous latex. The poor solubility of this catalyst in aqueous medium lowered its catalytic activity. Based on experimental observations presented in Chapter 4, direct in-situ synthesis of $RhCl(PPh_3)_3$ using aqueous catalyst precursor $RhCl_3$ and PPh_3 as well as the addition of alcohol improved both the diffusion of the catalyst and the in-situ synthesis efficiency which promote the hydrogenation reaction.

One would expect that the hydrogenation rate should be significantly increased if the catalyst itself could be separated from the NBR latex and transferred from the bulk water phase to the polymer particle phase. Guided by this idea, two water-soluble rhodium catalysts $RhCl(TPPMS)_3$ and $RhCl(TPPTS)_3$ were synthesized and used for NBR latex hydrogenation. The hydrogenation reaction conditions such as catalyst loading, temperature, hydrogen pressure were investigated and compared with $RhCl(PPh_3)_3/PPh_3$ catalytic system.

5.1 Introduction of water soluble catalyst

There is an increasing interest in carrying out catalytic reactions in aqueous media because of the environmental benign effect of using water as a solvent as well as its broad range of potential applications. Compared with conventional transition metal complexes (organometallics) which generally are insoluble in water, novel water-soluble metal complexes could improve its diffusion in aqueous media which may improve the efficiency of the catalyst. These metal complexes have been the subject of significant interest for many years. One of the most successful applications is for the biphasic hydrogenation/hydroformylation of small olefins ($< C_6$) as the catalyst offers the advantages of easy catalyst/product separation.

Meanwhile, water-soluble catalysts have also been studied for a large olefins ($>C_8$) or even unsaturated polymers in an aqueous system. The previous experimental results [48-50] showed that hydrogenation activity of the catalysts were substantially reduced as the length of the carbon chain increased. As a result, the desired conversion could not be achieved.

5.2 Experimental

Two types of NBR latices were used for hydrogenation in this chapter. The commercial NBR latex was provided by Lanxess Deutschland GmbH and the in-house NBR latex was synthesized in our lab via standard emulsion copolymerization.

5.2.1 NBR latex Hydrogenation

The hydrogenation reaction was still carried out in the same Parr reactor as described in Chapter 4. 100 mL NBR latex (with a certain amount of additives e.g. organic co-solvent, co-catalyst ligand) was added to the reactor. The catalyst was weighed in a glass bucket and placed in a catalyst addition device which was installed in the head of the reactor. After reaching the reaction temperature, catalyst was added to the NBR latex under H_2. The hydrogenated NBR latex was sampled at intervals during the reaction.

5.2.2 Characterization

The conversion was measured by FT-IR and ^1H NMR spectroscopy. The relative viscosity of NBR and the resultant HNBRs were also measured by Ubbelohde capillary viscometer. The metal concentration in polymer particles was measured by ICP-OES and the morphology of the NBR latex was measured by DLS. Detailed description of characterization procedures could be found in Chapter 3.

5.3 NBR latex hydrogenation using water-soluble rhodium catalysts

Initial results obtained from hydrogenating the commercial NBR latex in the presence of $RhCl(TPPMS)_3$ or $RhCl(TPPTS)_3$ catalysts, are presented in Table 5-1 and Table 5-2 respectively. For NBR latex hydrogenation using the $RhCl(TPPMS)_3$ catalyst, the residual C=Cs in NBR were continuously reduced in the course of the reaction and desired conversion was achieved at the end. The result of hydrogenation using $RhCl(TPPMS)_3$ was compared with that using $RhCl(PPh_3)_3$ catalyst in terms of reaction time. It can be see the reaction time is much shorter than using solid $RhCl(PPh_3)_3$ catalyst. In addition, it can be seen that $RhCl(TPPMS)_3$ could catalyze the NBR hydrogenation reaction at a relatively low temperature.

Table 5-1 NBR latex hydrogenation using $RhCl(TPPMS)_3$ catalyst

Entry	**$RhCl(TPPMS)_3$** (mmol/L)	**NBR latex** (g/L)	**[C=C]/[Rh]** molar ratio	**Time** (hrs)	**Conversion** (mol.%)
1	0.26	25	1100	22	90
2	0.52	50	1100	5	80
3	0.52	50	1100	8.5	95
4	1.04	50	550	6	97
5	1.04	100	1100	50	92

NBR Latex: commercial NBR latex (50g/L), total volume = 100 mL, T = 100 °C, P_{H_2} = 1000 psig

Then the activity of $RhCl(TPPTS)_3$ catalyst was tested for the same reaction. The hydrogenation results in Table 5-2 showed a different hydrogenation behavior when using the $RhCl(TPPTS)_3$. It was observed that the conversion slowly increased in the first several hours but leveled off thereafter. No desired conversion was found at the end of the reaction.

Since NBR latex could not be successfully hydrogenated using RhCl(TPPTS)$_3$, the following discussions mainly focus on NBR hydrogenation using the RhCl(TPPMS)$_3$ catalyst. The results obtained from RhCl(TPPTS)$_3$ are used for comparison.

Table 5-2 NBR latex hydrogenation using RhCl(TPPTS)$_3$ catalyst

Entry	RhCl(TPPTS)$_3$ (mmol/L)	NBR latex (g/L)	[C=C]/[Rh] molar ratio	Time (hrs)	Conversion (mol.%)
1	0.26	25	1100	20	20
2	0.52	50	1100	5	15
3	0.52	50	1100	10	19
4	0.52	50	1100	13	21
5	0.52	50	1100	20	22
6	1.04	100	1100	10	25
7	1.04	50	550	14	25

Commercial NBR latex = 50g/L, total volume = 100 mL, T = 100 ℃, P_{H_2} = 1000 psig

5.3.1 FT-IR analysis

A typical FT-IR spectrum of NBR hydrogenation using RhCl(TPPTMS)$_3$ is depicted in Figure 5-1. During the hydrogenation, the intensity of peaks at 970 cm^{-1} and 920 cm^{-1} considerably diminished while a peak at 723 cm^{-1} appeared. Similar to the NBR RhCl(PPh$_3$)$_3$ catalyst, RhCl(TPPMS)$_3$ also exhibited good chemoselectivity in hydrogenation. Only the C=C double bonds in the NBR were hydrogenated whereas the unsaturated C≡N groups were not affected during the hydrogenation.

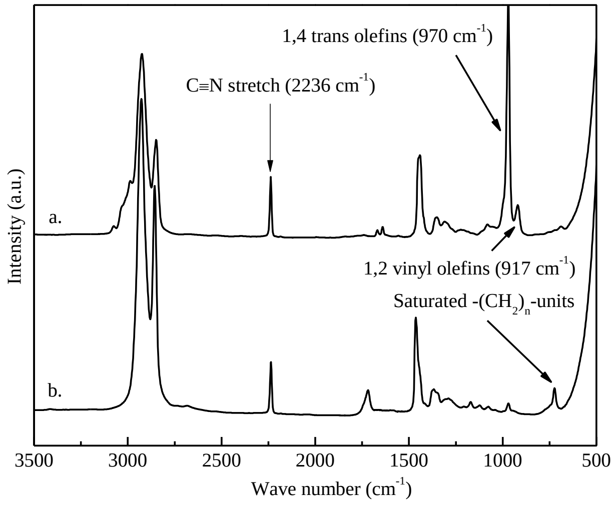


Figure 5-1 Typical FT-IR spectra of NBR and hydrogenated NBR

(a) NBR, (b) hydrogenated NBR (95 mol.%), NBR latex = 50 g/L, RhCl(TPPMS)$_3$ = 0.52 mmol/L, T = 100 ℃, P_{H_2} = 1000 psig

5.3.2 Measurement of relative viscosity

The solubility of the HNBR was measured by its dissolution in MCB solvent. For HNBR obtained using RhCl(TPPMS)$_3$ catalyst, it was soluble in MCB. However, it was observed that the dissolution process takes a longer time than that of using solid RhCl(PPh$_3$)$_3$/PPh$_3$ catalytic system. The relative viscosity (η_{rel}*) of HNBR products at the industrially required hydrogenation degree are listed in Table 5-3. It was found that the HNBR made by using RhCl(TPPMS)$_3$ possessed a large relative viscosity. This indicates a cross-linking reaction accompanied with the hydrogenation reaction.

Meanwhile, the solubility of HNBR product getting from RhCl(TPPTS)$_3$ catalyst were also tested. The resultant HNBR with low conversions (ca. 10 mol.%) could not be completely dissolved in MCB showing that the $RhCl(TPPTS)_3$ is more prone in activating cross-linking than the less water-soluble catalyst $RhCl(TPPMS)_3$ and oil soluble $RhCl(PPh_3)_3$.

Table 5-3 Viscosity results for yielded HNBR using different catalysts

Sample	Catalyst	Conversion (mol.%)	Relative Viscosity $\eta_{rel.}$*
HNBR[1]	$RhCl(PPh_3)_3/PPh_3$	95	3.65
HNBR[2]	$RhCl(PPh_3)_3/PPh_3$	95	3.85
HNBR[3]	$RhCl(TPPMS)_3$	95	4.45
HNBR[3]	$RhCl(TPPTS)_3$	22	gelled

[1] HNBR from NBR solution hydrogenation (commercial HNBR was provided by Lanxess Deutschland GmbH)

[2] HNBR from NBR latex hydrogenation: commercial NBR latex = 50 g/L, $RhCl(PPh_3)_3$ = 0.52 mmol/L, PPh_3 = 18 mmol/L, T = 145 ℃, P_{H_2} = 1000 psig

[3] HNBR from NBR latex hydrogenation: commercial NBR latex = 50 g/L, $RhCl(TPPMS)_3$ or $RhCl(TPPTS)_3$ = 0.52 mmol/L, T = 100 ℃, P_{H_2} = 1000 psig

5.3.3 The diffusion of the catalyst in NBR latex hydrogenation

Although the catalyst can be presented in the aqueous phase, at the water-polymer interface or in the polymer phase, it has been shown in the Chapter 4 that catalyst diffusion inside the polymer phase is crucial for achieving required high conversions.

The distribution of the catalyst during the NBR latex hydrogenation could be easily detected by the color of the aqueous phase and the polymer phase. In the hydrogenation experiments using $RhCl(TPPTS)_3$ catalyst, it remained in the aqueous phase as evidenced by the red aqueous phase after separating the NBR polymer. However, the precipitated polymer became a little bit dark after the reaction. This is probably when the catalyst molecule diffuses toward the surface of the polymer particles, the water-soluble ligands tend to stay in the aqueous phase while the metal center of the catalyst may be attracted on the aqueous/polymer inter phase or even diffuse into the polymer phase. Hence, the water-soluble ligands may dissociate from the metal center to remain in the aqueous phase, and the residual transition metal complex promoted the cross-linking when it came in contact with the NBR.

With $RhCl(TPPMS)_3$, the aqueous phase of the HNBR latex was almost colorless while the resultant HNBR was orange-yellow, showing the catalyst was extracted into the polymer phase during the reaction. This result was in marked contrast to the hydrogenation of small organic molecules or the biphasic hydrogenation of polymers with $RhCl(TPPMS)_3$ where the catalyst always retained in the aqueous phase after the reaction [50, 101]. Therefore, in order to provide sufficient qualitative evidence for the distribution of catalysts during the reaction, the rhodium metal concentration in the polymer was carefully measured via polymer digestion and ICP analysis.

Compared to analyzing the residual catalyst concentration in the aqueous phase, direct measurement of the catalyst in the polymer could give us more accurate information about the catalyst diffusion process during the hydrogenation reaction (Figure 5-2). Only small amounts of rhodium are detected in polymers after the reaction using the $RhCl(TPPTS)_3$ catalyst. The trisulfonated PPh_3 ligand (TPPTS) based rhodium catalyst could be easily dissolved in the aqueous phase. The very small catalyst leaching of this catalyst in the biphasic hydrogenation or hydroformylation reported in the literatures showed that the TPPTS ligand based rhodium catalyst is prone to stay in the aqueous phase. Therefore, it has also been described that hydrogenation of poly-diene in aqueous micelles system with a Rh/TPPTS catalyst showed a dramatically decreased reaction rate and conversion with increase of polymer molecular weight [48].

To the contrary, the distribution of the $RhCl(TPPMS)_3$ in the hydrogenation of high molecular weight polymer in the aqueous micelles system is quite different from $RhCl(TPPTS)_3$ and more than half of the feed catalyst diffused into the polymer particles during the reaction. Although there is no research focused on hydrogenation using the RhCl(TPPMS)$_3$ catalyst in a aqueous micelle system, the low solubility of the catalyst as well as the strong coordination between the polymer substrate and the catalyst might have caused phase transfer of the catalyst during the aqueous micelle hydrogenation reaction [102].

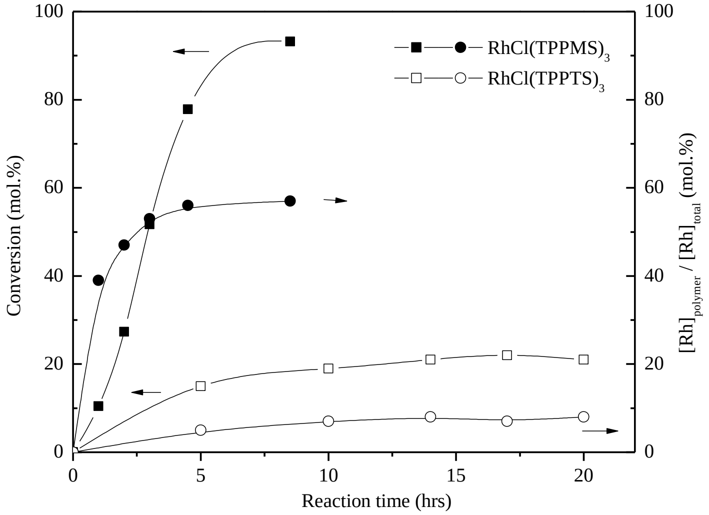


Figure 5-2 The change of rhodium concentration in NBR polymer particles throughout hydrogenation

Commercial NBR latex = 50 g/L, Rh catalysts = 0.52 mmol/L, total volume = 100 mL,
T = 100 ℃, P_{H_2} = 1000 psig

5.3.4 The effects of reaction temperature, pressure and co-catalyst ligand on NBR latex hydrogenation using RhCl(TPPMS)$_3$

The effect of the reaction temperature, pressure and the co-catalyst ligand on the extent of hydrogenation conversion were studied using RhCl(TPPMS)$_3$. These results are summarized in Table 5-4, Figure 5-3, Table 5-5 and Table 5-6 respectively.

The hydrogenation reaction was studied in the range of 70 ℃ to 130 ℃ at a constant reaction pressure of 1000 psig with 0.52 mmol/L of catalyst loading. The agitation speed keeps at 1000 rpm. The conversion of NBR for a 9 hour reaction time at different temperatures is given in Figure 5-3. The results clearly show that the hydrogenation reaction is very sensitive to the temperature. From 70 ℃ to 100 ℃, the extent of hydrogenation greatly increased with the increase in temperature. The highest conversion (95 mol.%) was observed at 100 ℃. At higher temperatures the conversion decreased. This is probably due to the occurrence of catalyst deactivation at those temperatures.

Table 5-4 Effect of the temperature on the conversion of NBR after 9 hrs reaction time

Entry	**Temperature** ℃	**Conversion** (mol.%)	**TON** (h^{-1})
1	70	12	14.7
2	85	74	90.4
3	100	95	116.1
4	115	87	106.3
5	130	60	73.3

Commercial NBR latex = 50 g/L, total volume = 100mL, RhCl(TPPMS)$_3$ = 0.52 mmol/L, P_{H_2} = 1000 psig

TON: The molar number of C=Cs hydrogenated by one molar catalyst in unit time, measured at 95 mol.% conversion

This assumption is further confirmed by considering the NBR hydrogenation profiles (Figure 5-3). The initial reaction rate is highest at the highest temperature (130 ℃). However, after 2 hours, a rapid decay of catalyst activity is observed, likely due to catalyst deactivation. Similar observations were reported for related hydrogenations using the water-soluble catalyst systems [103, 104] indicating that the stability of the Rh/TPPMS catalyst is limited, though the temperature at which deactivation occurs to a considerable extent seems to be reaction-specific. In our NBR latex system, the optimum temperature for the hydrogenation of NBR latex was found to 100 ℃ under our reaction conditions.

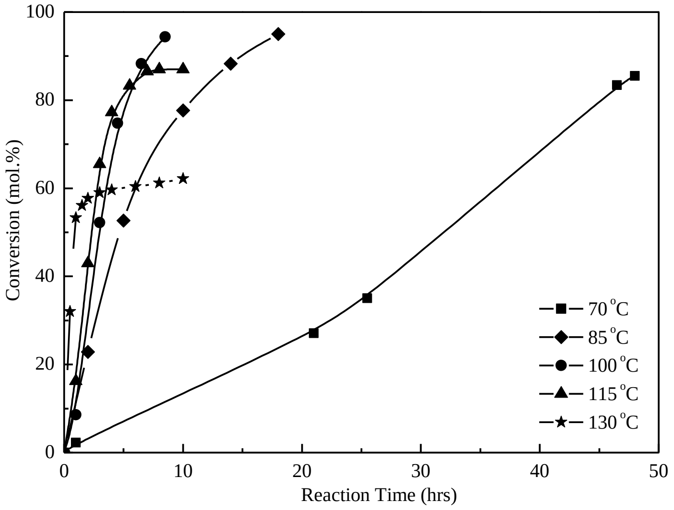


Figure 5-3 NBR conversion versus time under different temperature

Commercial NBR latex = 50 g/L, total volume = 100 mL, $RhCl(TPPMS)_3$ = 0.52 mmol/L, P_{H_2} = 1000 psig

It has been described that the hydrogenation of NBR in polymer solution using $RhCl(PPH_3)_3$ or $RhH(PPh_3)_4$ exhibits a first- to zero-order dependence on hydrogen pressure as the system pressure increase [95]. The influence of hydrogen pressure was also examined here and the results are shown in Table 5-5. Similar behavior was observed in our latex reaction system using $RhCl(TPPMS)_3$ catalyst. As the hydrogen pressure was varied over the range of 400 psig to 1000 psig, it was found the hydrogenation rate increased with increasing hydrogen pressure. However, no significant improvement on the catalytic performance of $RhCl(TPPMS)_3$ was observed when hydrogen pressures exceeded 1000 psig.

Table 5-5 The effect of pressure on NBR latex hydrogenation using RhCl(TPPMS)$_3$

Entry	**Pressure** (psig)	**Conversion** (mol.%)	**TOF** (h^{-1})
1	400	50	61
2	600	78	95
3	800	92	112
4	1000	95	116
5	1200	96	117

Commercial NBR latex (50 g/L), total volume = 100 mL, RhCl(TPPMS)$_3$ = 0.52 mmol/L, reaction time = 9 hours

TON: The molar number of C=Cs hydrogenated by one molar catalyst in unit time, measured at 95 mol.% conversion

Table 5-6 The effect of and co-catalyst ligand on NBR latex hydrogenation

Entry	**Added TPPMS/Catalyst ratio** (mol./mol.)	**Time** (hrs)	**Conversion** (mol.%)	**TOF** (h^{-1})
1	3:1	15	95	70
2	10:1	32	95	33
3	35:1	100	95	11

Commercial NBR latex (50 g/L), total volume = 100 mL, RhCl(TPPMS)$_3$= 0.52 mmol/L, P_{H_2} = 1000 psig, T = 100 ℃

TON: The molar number of C=Cs hydrogenated by one molar catalyst in unit time, measured at 95 mol.% conversion

It was mentioned in Chapter 4 that the co-catalyst ligand PPh$_3$ greatly affected NBR latex hydrogenation as it facilitated the transportation of the RhCl(PPh$_3$)$_3$ catalyst. Although the addition of TPPMS is not required when using RhCl(TPPMS)$_3$ for NBR latex hydrogenation, the effect of the co-catalyst ligand TPPMS to the catalyst RhCl(TPPMS)$_3$ ratio was still examined here. It was found that the NBR latex hydrogenation reaction is strongly influenced by the amount of TPPMS added to the rhodium precursor (Table 5-6). The highest catalytic activity was observed for the catalyst without the addition of co-catalyst ligand. Once the co-catalyst ligand TPPMS was added, the activity dramatically decreased. This has been reported that the competition between the added free TPPMS ligand and the C=C units of NBR for a coordination site on the rhodium led to a retardation in the activation of the hydrogenation reaction [105].

5.3.5 Influence of the organic co-solvent

Five different organic solvents (mono-chlorobenzene, toluene, acetone, methyl ethyl ketone and ethanol) were examined and are presented in relation with the final hydrogenation degree and TOF of the respective hydrogenation reactions. Figure 5-4 showed that the hydrogenation of the NBR latex using $RhCl(TPPMS)_3$ is also solvent dependent.

Firstly, it is worth mentioning that the catalytic system performed to a sufficient catalytic activity (TOF 117 h^{-1} at 95 mol.% conversion) without the presence of an organic solvent. When adding mono-chlorobenzene or toluene as co-solvent to the system, the hydrogenation activity of the catalyst decreased and high conversions (95 mol.%) could not be achieved. MCB and toluene are good solvent for NBR polymer but immiscible with water. When adding this type of co-solvent into the NBR latex, the NBR particles were swelled by co-solvent which could prevent the water-soluble catalyst from contacting the C=Cs in NBR.

Different from MCB and Toluene, MEK and acetone are compatible with NBR latex system. They are miscible with water, catalyst and NBR. The presence of this type of organic co-solvents could also swell the NBR. Different from MCB or toluene, this type of co-solvent facilitates the approach of the catalyst to the bulk hydrophobic interior region of the swollen polymer. As a result, high conversion and activities were observed with the addition of this type of co-solvent.

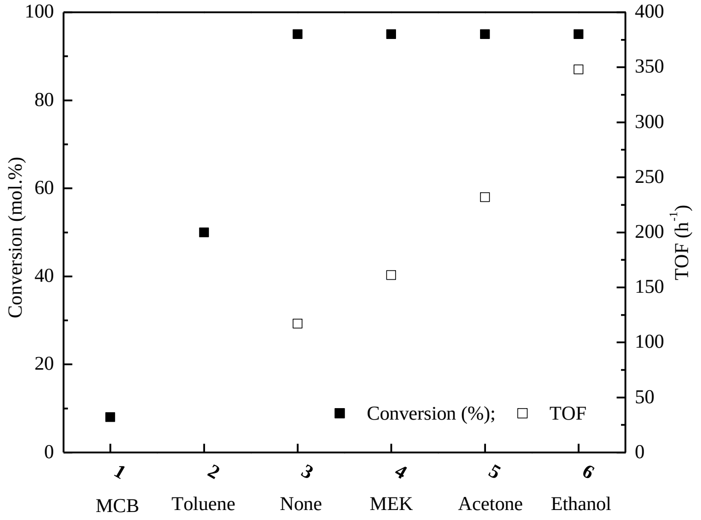


Figure 5-4 Influence of organic solvent in the hydrogenation of NBR latex

Commercial NBR latex = 50 g/L, co-solvent/NBR latex = 1/10 (vol./vol.),
$RhCl(TPPMS)_3$ = 0.52 mmol/L, T = 100 ℃, P_{H_2} = 1000 psig)

The highest activity observed for NBR latex hydrogenation was with the addition of ethanol and is not something to be expected (Figure 5-5). It probably due to the following factors: (i) when alcohol diffused into the micelle, it can counter balance the charges and reduce the electrical repulsion in the stern layer of the micelles. In other words, the charge density at the micelles surface decreased and thereby the absolute value of the electrical potential was also reduced. Similar results have been reported by Li et al. when they added the alcohol in 1-dodecene hydroformylation in a biphasic catalytic system [100]; (ii) the presence of alcohol functions as a reducing agent which stabilizes the $RhCl(TPPMS)_3$ catalyst.

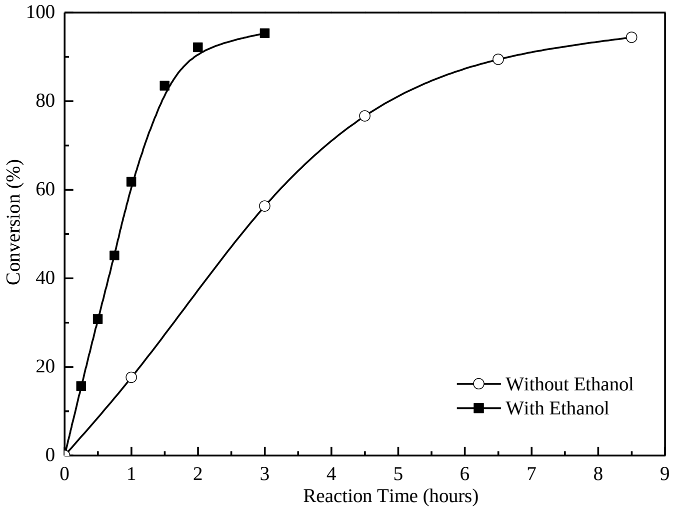


Figure 5-5 NBR latex hydrogenation by RhCl(TPPMS)$_3$ with ethanol addition

■ : NBR latex = 50 g/L, RhCl(TPPMS)$_3$ = 0.52 mmol/L, T = 100 ℃, P_{H_2} = 1000 psig

○: NBR latex = 50 g/L, ethanol/NBR latex = 1/10 (vol./vol.), RhCl(TPPMS)$_3$ = 0.52 mmol/L, T = 100 ℃, P_{H_2} = 1000 psig

5.4 Hydrogenation of In-house NBR latex

Singha et al. first studied the NBR latex hydrogenation using the same RhCl(TPPMS)$_3$ catalyst. It was reported that only 60 mol.% hydrogenation could be achieved (75 ℃ and 1 atmosphere hydrogen pressure) [49]. However, under our initial investigations, the hydrogenation degree could reach more than 95 mol.% without visible gel. In order to confirm our findings, different types of NBR latex were tested for hydrogenation using the RhCl(TPPMS)$_3$ catalyst.

As we know, the commercial NBR latex contains many additives (e.g. antioxidant, stabilizer) which are not necessary for a standard emulsion co-polymerization. To eliminate the possible effects from these materials, simple “in-house” NBR latices were synthesized and used for NBR latex hydrogenation using the RhCl(TPPMS)$_3$ catalyst.

5.4.1 Preparation of in house NBR latex

In house NBR latices were prepared by emulsion polymerization. In order to obtain NBR latex with different particle sizes and molecular weights (gel free or gelled), the surfactant to monomer ratio, the amount of chain transfer reagent, the polymerization time and temperature were varied and the recipes are summarized in Table 5-7 and Table 5-8. The particle size in the latex were determined by both dynamic light scattering (DLS) and transmission electron microscopy (TEM), while the molecular weight of the gel-free NBR was determined by GPC. All the other properties of NBR were measured according to the methods provided in Chapter 3.

Table 5-7 Recipes used for the preparation of NBR latex with small particle size

Components (g)	NBR-MP-GF	NBR-SP-GF	NBR-SP-G
1,3-butadiene	27	27	27
Acrylonitrile	13	13	13
Potassium persulfate	0.1	0.1	0.1
Sodium oleate	1	2	0.5
Deionized Water	80	80	80
t-DDM (g)	0.19	0.10	-
Temperature (℃)	30	30	50
Particle size (nm)	80	42	53
Conversion (%)	57	65	84
Solid content (wt.%)	13	15	17
CN (mol.%)	41	40	38
Gel	No	No	Yes

NBR-MP-GF: Gel free NBR latex with medium size particle. Mn = 103,391 (± 3%) g/mol, PDI = 2.9

NBR-SP-GF: Gel free NBR latex with small particle. Mn = 75,610 (± 3%) g/mol, PDI = 2.5

NBR-SP-G: Gelled NBR latex with small particle.

Table 5-8 Recipes used for the preparation of NBR latex with large particle size

Components (g)	NBR-LP-GF	NBR-LP-G
1,3-butadiene	42 (27g)	42 (27g)
Acrylonitrile	16 (13g)	16 (13g)
Potassium persulfate	0.1	0.1
Sodium oleate	0.4	0.02
Deionized Water	80	80
Chain transfer reagent (g)	0.19	-
Temperature (℃)	30	30
Particle size (nm)	137	160
Conversion (%)	60	81
Solid content (wt.%)	14	20
CN (mol.%)	40	40
Gel	No	Yes

NBR-LP-GF: Gel free NBR latex with large particle size. Mn = 210,323 (±5%) g/mol, PDI = 2.8
NBR-LP-G: Gelled NBR latex with large particle size.

5.4.2 Characterization of in house NBR

The compositions and microstructures of the NBRs were first determined by FT-IR. Figure 5-6 shows a typical spectrum of in- house synthesized NBR. The distinct peak exhibited at 2236 cm^{-1} shows the existence of nitrile group (C≡N) in the co-polymer. Due to the existence of two C=C double bonds, the polymerization of 1,3-butadiene usually gives rise to different configurations. The intense peak shown at 969 cm^{-1} belongs to the vibration of the 1,4-trans double bonds while the small absorbance at 910 cm^{-1} corresponds to the 1,2-vinyl terminal bonds, which is much weaker than that of 1,4-trans double bonds.

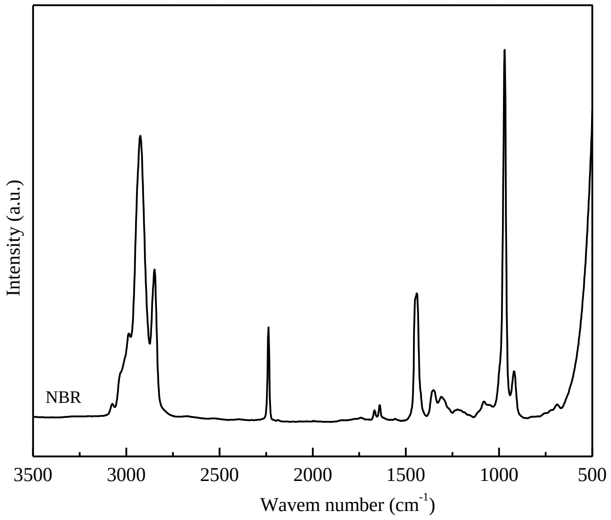


Figure 5-6 Typical FT-IR spectral of in-house NBR

In house NBR latex: NBR-SP-GF, average particle size measured by DLS is 42 nm.

The effect of polymerization reaction condition greatly affected formed NBR especially in its micro-structure. Figure 5-7 and Figure 5-8 show typical ^{1}H NMR spectra of NBRs with different structure (gel or gel free). For the gel-free NBR, aliphatic protons display signals between 0.9 and 2.8 ppm and the multiple peaks around 2.58 ppm indicates the presence of the acrylonitrile units. The peaks appearing in the region of 4.9-5.1 ppm are assigned to the 1,2-vinyl terminal units and the double peaks exhibited in the vicinity of 5.5 ppm are attributed to the protons of 1,4-olefin units. Figure 5-8 shows the NMR results of a highly gelled NBR. Due to the very low solubility of the NBR, it can be seen that broad peaks were observed.

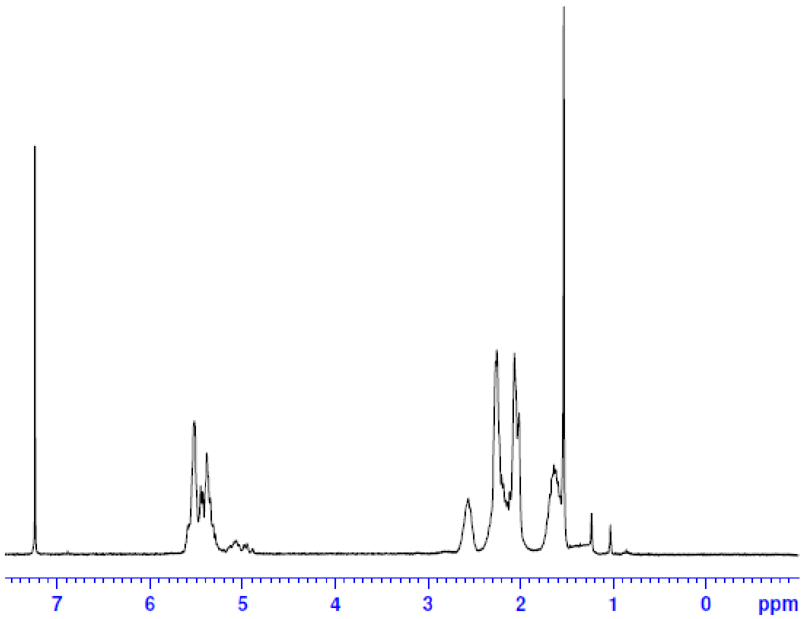


Figure 5-7 ^{1}H NMR spectral of in house NBR (Gel free)

In house NBR latex: NBR-SP-GF, average particle size measured by DLS is 42 nm. The polymerization reaction condition is summarized in Table 5-7

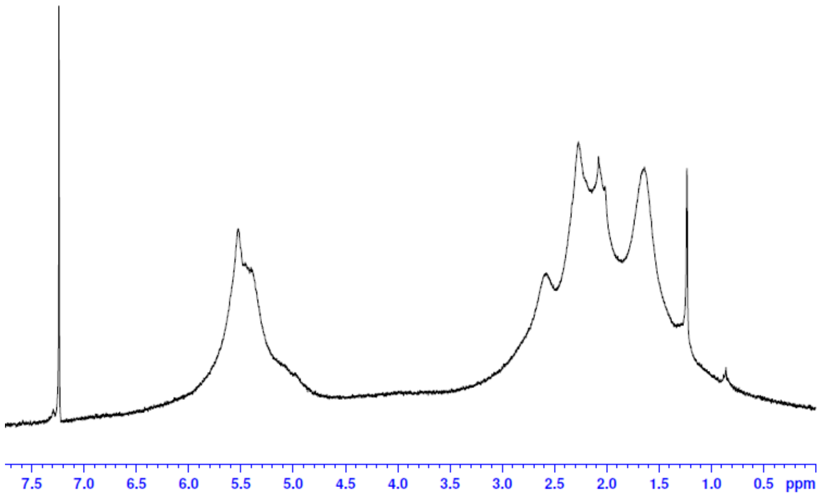


Figure 5-8 ^{1}H NMR spectral of in house NBR (Gelled)

In house NBR latex: NBR-SP-G, average particle size measured by DLS is 53 nm. The polymerization reaction condition is summarized in Table 5-7

5.4.3 Hydrogenation of commercial and in house NBR latex

In commercial NBR latex, there are a variety of compounds e.g. stabilizer and anti-oxidant that could be poisonous to catalysts. It has been reported by Wei that these impurities within the commercial polymer latex could affect the latex hydrogenation or even kill some types of catalysts [76].

Therefore, we studied the behavior of $RhCl(TPPMS)_3$ catalyst for the hydrogenation reaction of the in house NBR latex. The results are presented in Figure 5-9. The hydrogenation behavior (hydrogenation curve and final conversion) remained practically unchanged for both NBR lattices which demonstrates that under our operational conditions, the $RhCl(TPPMS)_3$ catalyst is tolerant to impurities in the commercial polymer latex.

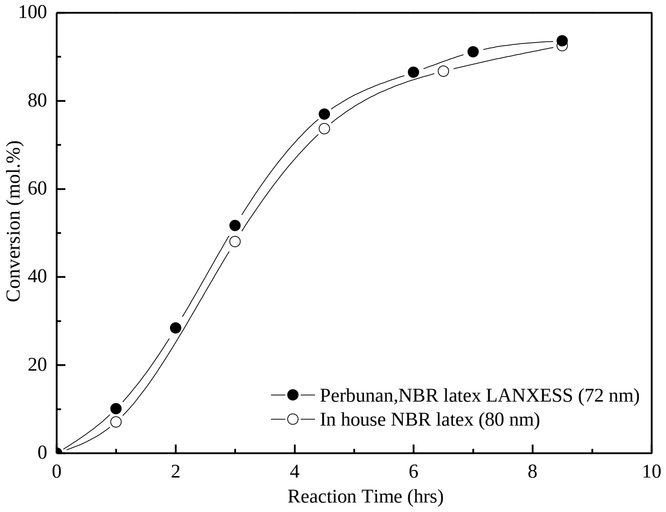


Figure 5-9 NBR latices hydrogenation by $RhCl(TPPMS)_3$

Commercial or in house NBR latex = 50 g/L, $RhCl(TPPMS)_3$ = 0.52 mmol/L, T = 100 ℃, P_{H_2} = 1000 psig

5.4.4 The effect of particle size on NBR latex hydrogenation

First of all, the effect of particle size was studied for hydrogenation of gel free NBR latices (Table 5-9). Three gel-free NBR latices with particle size of 42 nm, 80 nm and 137 nm were used in the investigation. The hydrogenation conditions such as the molar ratio of the catalyst to the C=C double bonds in the NBR latex, temperature, hydrogen pressure were kept the same.

It was observed that reducing the latex particle size improves hydrogenation efficiency. With a small particle size, the hydrogenation reaction rate is fast. As we know, the catalyst was added in the aqueous phase and it needs to first contact the polymer particles before diffusing to the inside. With the same solid content, the NBR with a smaller particle size has a relative large total surface area and more $RhCl(TPPMS)_3$ catalyst could be contacted and diffused into the polymer particles quickly. Another possible factor that could influence the reaction rate is the short distance for the diffusion of the catalyst from the surface to react with double bonds residing in the inner part of the particles due to the smaller particle size.

Table 5-9 The effect of particle size on NBR latex hydrogenation

NBR latices	Particle Size (nm)	Time (hrs)	Conversion (mol.%)	TOF (h^{-1})
NBR-SP-GF	42	6	95	174
NBR-MP-GF	80	9	95	116
NBR-LP-GF	137	16	95	66

In house NBR latex = 50 g/L, $RhCl(TPPMS)_3$ = 0.52 mmol/L, T = 100 ℃, P_{H_2} = 1000 psig

TON: The molar number of C=Cs hydrogenated by one molar catalyst in unit time, measured at 95 mol.% conversion

5.4.5 The effect of molecular weight on NBR latex hydrogenation

In addition, the effect of molecular weight of NBR was also investigated (Table 5-10). It has been reported by El-Aasser et al. that the molecular weight of the polymer could greatly affect the hydrogenation reaction in the polymer latex hydrogenation [106]. Since the hydrogenation reactions take place during the process in which hydrogenation catalyst diffused from the particles surface into the interior of the particles, a relatively highly hydrogenated layer could form close to the particle surface. However, for the polymer with a small molecular weight (gel free), the diffusion of the small polymer chains occur all at the time which would diminish the formation of the layers.

Hydrogenation reactions were initially carried out on NBR lattices with small particle in which the average particle size was between 40 and 55 nm. With different reaction temperature and the addition of chain transfer reagent, the molecular weights of the in house NBRs were different. The gel free NBR latex used in the reaction has a molecular weight of 75,610 (Mn) with a PDI around 2.5 while the gelled NBR in the NBR latex is highly cross-linked and the molecular weight could not be directly measured.

Table 5-10 shows the degree of hydrogenation in each hydrogenation process. Although the mobilities of polymer chains in the latex particles for these latices are expected to be quite different, it seems that a high gel fraction does not exert much influence on the small particle. High degrees of hydrogenation were still attained under similar reaction times (6 hrs vs. 6.5 hrs) in both NBR latices showing (i) the particle size is small enough for the catalyst to diffuse from the surface to the center of the particle (ii) the diffusion of the catalyst is fast under the reaction temperature and the hydrogenation of latex was mainly a reaction controlled process. Therefore, a homogeneous model was proposed for this case.

For NBR latices with much larger particle sizes, the degree of hydrogenation and the reaction rates were quite different within the different NBR latices (Table 5-10). In the gel free NBR latex, the diffusion of the soft NBR chains inside of the particles occurs all the time. For the gelled NBR latex, only 45 mol.% conversion could be achieved. Since the diffusion of polymer chains is very limited, the result indicates that the catalyst could not diffuse to contact all of the double bonds in the particles. The hydrogenation of latex with large particle size was a diffusion controlled process.

Table 5-10 The effect of molecular weight on NBR latex hydrogenation

Entry	**Particle Size** (nm)	**Gel**	**Time** (hrs)	**Conversion** (mol.%)	**TOF** (h^{-1})
1	42	No	6.0	95	174
2	53	Yes	6.5	95	161
3	137	No	16	82	56
4	160	Yes	22	45	23

In house NBR latex = 50 g/L, $RhCl(TPPMS)_3$ = 0.52 mmol/L, T = 100 ℃, P_{H_2} = 1000 psig

5.5 Conclusions

It was known from the previous NBR 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 catalysts transfer from the bulk water phase onto the particle surface, two types of water-soluble rhodium catalyst, $RhCl(TPPMS)_3$ and $RhCl(TPPTS)_3$, were tried for the latex hydrogenation in this study.

When the hydrophilic $RhCl(TPPTS)_3$ catalyst was used, the catalyst could not diffuse into the polymer particles and achieve the required hydrogenation. However, using the $RhCl(TPPMS)_3$ catalyst, the catalyst could easily diffuse into the polymer particles by itself and hydrogenation reaction was achieved. Compared with $RhCl(PPh_3)_3/PPh_3$ catalytic system, the reaction could be carried out under lower temperature (100 ℃) and no co-catalyst was required during the reaction.

In-house NBR latex was synthesized via emulsion polymerization and compared with the commercial NBR latex. It was found the hydrogenation behaviors were similar using these NBR latices. Beside, the effect of particle size and the molecular weight of the NBR in the latex were investigated. The gel fraction in the latex particles does not influence the diffusion of the catalyst very much, but greatly affects the mobility of the polymer chains within the particles.

Chapter 6

NBR latex hydrogenation with second generation of Grubbs catalyst

The present chapter reports on our findings of the hydrogenation of NBR latex catalyzed by a ruthenium based catalyst: second generation of Grubbs catalyst.

6.1 Introduction

Although the rhodium based catalytic systems such as $RhCl(PPh_3)_3/PPh_3$ and $RhCl(TPPMS)_3$ have been proven to be effective for NBR latex hydrogenation, one of the drawbacks with these catalysts is the relatively high cost of Rh metal. This issue attracts more concerns when high catalyst loading is required. To circumvent this cost problem, one feasible solution is to develop new catalysts based on relative cheaper metals than Rh. Catalysts based on other cheaper platinum group transition metals have been utilized previously for hydrogenation of diene-based polymers. Different osmium and ruthenium based catalysts have activity for NBR hydrogenation in solution systems [27, 107]. However, very little research has been conducted on using these catalysts in NBR latex systems. Guo and Rempel studied several ruthenium based catalysts in the hydrogenation of NBR latices [42]. It was found $RuCl_2(PPh_3)_3$ is the most activity catalyst and 95 mol.% conversion could be achieved. Wei tested the $OsH(CO)(PCy_3)_2$ catalyst for direct NBR latex hydrogenation [108] and the final conversion could be achieved to 90 mol.% under mild reaction condition (e.g. 1 wt.% catalyst loading, 100 ℃, 800 psig of H_2). However, in all these reactions, the addition of a large amount of organic co-solvent was required. In the meantime, gels were also observed in the final HNBR products.

Ruthenium carbene complexes have been wildly used in organic synthesis to achieve olefin cross-metathesis (CM), ring-opening metathesis polymerization (ROMP), and ring-closing metathesis (RCM) [109]. Due to their high activity and easy of handling, they've been adopted in many commercial applications such as cross metathesis to make natural products [110], functionalization of vinyl terminated polyolefin [111] and dicarboxylic acid production [112]. In addition, this type of catalysts also showed activity on several other reactions such as hydrogenation, Suzuki coupling with suitable substrates and under certain reaction conditions [113]. In the last decade, several research groups have developed multiple reaction processes using Grubbs-type catalysts [114-117].

With these previous successful examples, we attempted the Grubbs type ruthenium carbene catalysts in our NBR latex hydrogenation research. In the present study, Grubbs second generation catalyst (G2) is first dissolved in tiny amount of organic solvent which was further mixed with NBR latex for hydrogenation reaction. The conversions as well as the gel formation were monitored through the reaction. As the core of this research, the hydrogenation performance of the G2 catalyst will be our major concerns. The metathesis activity of G2 catalyst is observed during the reaction. It affects the molecular weight of the NBR/HNBR. In addition, the relationship between metathesis and hydrogenation is also briefly explained based on our experiment results.

6.2 Experimental

6.2.1 Catalyst solution preparation

The Grubbs second generation catalyst solution was prepared in a glove box. The weighed G2 catalyst was dissolved in certain amount of MCB organic solvent and then the catalyst solution was transferred to the catalyst adding device which was connected to the reactor.

6.2.2 Mixed metathesis and hydrogenation of NBR in latex

Metathesis and hydrogenation of NBR latex was carried out in a 300 mL Parr reactor. The NBR latex with chain transfer agent (CTA) 1-hexene were added to the reaction and deoxygenated by purging the system with nitrogen gas and the system was heated to the reaction temperature. After that, the G2 catalyst solution prepared in a glove box was injected into the reactor under high pressure H_2 gas. The hydrogen pressure and reaction temperature were kept constant throughout the reaction period. The reaction time was recorded and the hydrogenated NBR latex was sampled at different reaction times.

6.2.3 Tandem metathesis and hydrogenation of NBR in latex

The term tandem catalysis is used to describe coupled catalyses in which sequential transformation of the substrate occurs via two (or more) mechanistically distinct processes. Generally, two of the accepted meanings for the word tandem reaction in chemistry are: (a) “an arrangement of two [mechanisms] working in cooperation”, and (b) “one after the other”.

Here, the tandem metathesis hydrogenation reaction was still carried out in a 300 mL Parr reactor. After degassing, the temperature was first set to the room temperature and the G2 catalyst solution was injected into the NBR latex under N_2 gas. During the metathesis reaction period, NBR latex samples were taken from the reactor at different times and the molecular weight of the NBR was measured by GPC. After several hours, the reactor was heated up to the desired hydrogenation temperature and hydrogen gas was added to the reactor for hydrogenation reaction. The hydrogenated NBR latex was also sampled at different intervals.

6.2.4 Characterization

The hydrogenation degree was measured by FT-IR spectroscopy. The molecular weight of the metathetically degraded NBRs and the hydrogenated NBRs were measured by GPC. The differential index of reflection (dn/dc) for pure NBR and HNBR (99 mol.% conversion) is 0.075 and 0.105 respectively. The dn/dc value for partially hydrogenation is calculated as:

$$\mathbf{dn/dc(x mol.\%\ HNBR) = x/100*0.105 + (100-x)/100*0.075}$$

Detailed characterization procedures for FT-IR and GPC have been described in Chapter 3.

6.3 Results and discussion

6.3.1 The dispersion of Grubbs 2nd catalyst in NBR latex

As we discovered in the previous chapters, the dispersion of the catalyst in the latex system is a crucial step for hydrogenation, especially for achieving the required high conversion.

Similarly to $RhCl(PPh_3)_3$, the hydrophobic Grubbs second generation catalyst couldn't be well dispersed in an aqueous latex system by catalyst itself (experimental observations). For $RhCl(PPh_3)_3$ catalyst, PPh_3 was used to transport it in the NBR particles in the latex. However, PPh_3 could not be used for G2 catalyst since it would kill the activity of the catalyst [118]. Therefore, the addition of a small amount of organic solvent improves the catalyst dispersion and mass transfer processes. Therefore certain organic solvent was added to facilitate the catalyst diffusion in NBR latex. Among different kinds of organic solvents, MCB has been found as a good solvent for NBR hydrogenation [94] and it was selected as a solvent in our research.

6.3.2 NBR latex metathesis/hydrogenation

The representative metathesis/hydrogenation of NBR in latex was carried out under the reaction condition of 0.287 mmol/L G2 catalyst loading with 80 mmol/L of 1-hexene, at 100 ℃ and 1000 psig hydrogen. The reaction result is shown in Figure 6-1. In the profile, the hydrogenation conversion goes up with the reaction time. However, it was also observed that the hydrogenation conversion plot exhibits an S-curve characteristic with a small induction period.

The quality of the HNBRs regarding the gel formation was also monitored. A very important finding here is that the resultant HNBR could be easily dissolved in MCB. This is quite different from the previous reported results when using conventional ruthenium catalysts for NBR solution/aqueous emulsion hydrogenation. The molecular weights of HNBRs at different hydrogenation conversion were able to be directly measured by GPC and the molecular weight change versus conversion result is shown in Figure 6-2. It can be seen that the change of molecular weight behaves differently during the reaction. It first decreased when the conversion is less than 20 mol.%. After that, the molecular weight gradually increased with the conversion. Compared to the original NBR, final molecular weight of the HNBR didn't change greatly which indicates that gel was not substantially formed during the reaction.

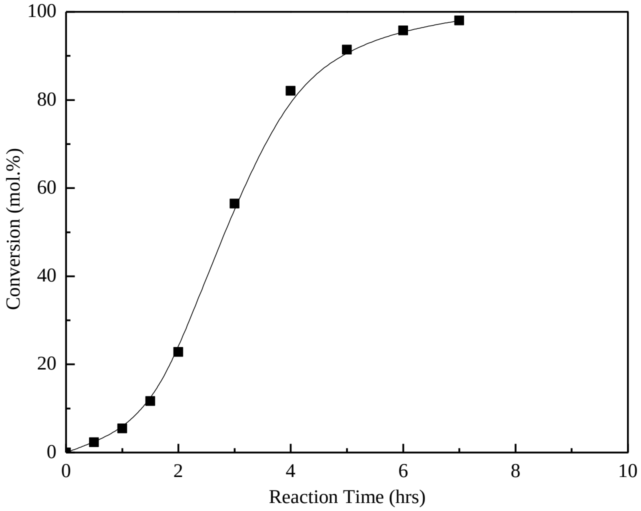


Figure 6-1 NBR latex metathesis/hydrogenation under G2 catalyst

Commercial NBR latex (50 g/L), total volume = 100 mL, G2 = 0.287 mmol/L, NBR latex/MCB = 12.5 (vol./vol.), T = 100 ℃, P_{H_2} =1000 psig

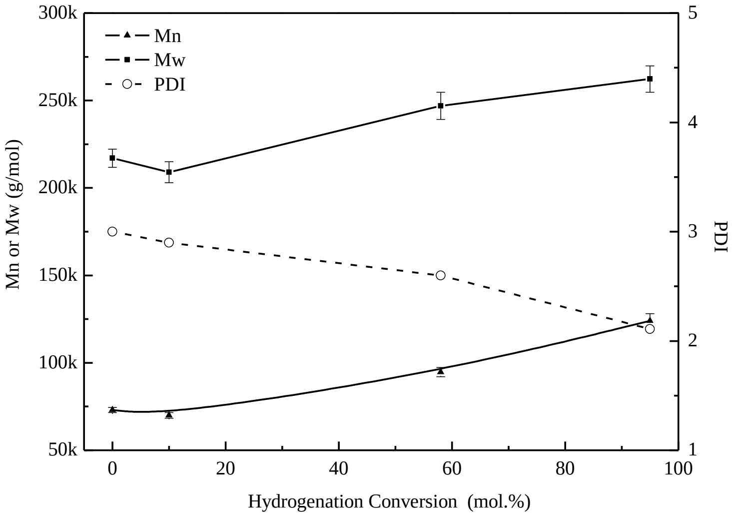


Figure 6-2 The average molecular weight of NBR in direct NBR latex hydrogenation under G2 catalyst

Commercial NBR latex (50 g/L), total volume = 100 mL, G2 = 0.287 mmol/L, NBR latex/MCB = 12.5 (vol./vol.), T = 100 ℃, P_{H_2} =1000 psig

6.3.3 Tandem metathesis and hydrogenation of NBR latex

In order to better understand the multiple reactions under the previous reaction process using G2 catalyst, the tandem metathesis hydrogenation reaction was performed for comparison. In this experiment, an extended time (ca. 3 hours) was provided for the metathesis reaction only. Since hydrogen gas wasn't added into the reactor in that period of time, only metathesis reaction occurred.

The extension of metathesis reaction was reflected by the molecular weight of NBR and results using the G2 catalyst are depicted in Figure 6-3. First, we can see the molecular weight of NBR decreased in the first 3 hours. Although the molecular weight change is limited, it keeps reducing in the metathesis period. This result is in a good agreement with the character of metathesis depolymerization reaction. In the figure, the number average of molecular weight (Mn) slightly decreased while the weight average of molecular weight (Mw) clearly dropped. The kind of change leads to a relative narrow distribution of molecular weight which is represented by polydispersity index (PDI) in the figure. After adding the hydrogen gas, no further reduction of molecular weight was observed. Instead, both the Mn and Mw started to increase. The additional reaction period extended the metathesis reaction between NBR and CTA. It can be seen from Figure 6-3 that the decrease of molecular weight is much more evident in this tandem metathesis hydrogenation reaction.

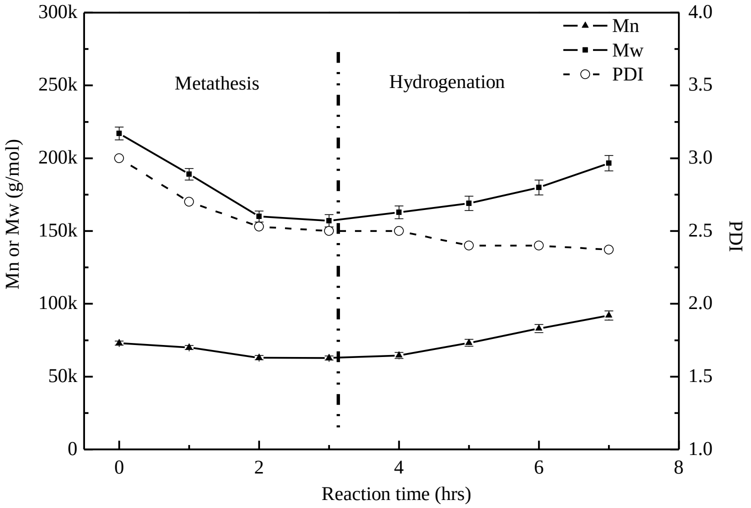


Figure 6-3 The average molecular weight of NBR in NBR latex tandem metathesis hydrogenation under G2 catalyst

Commercial NBR latex (50 g/L), total volume = 100 mL, G2 = 0.287 mmol/L, 1-hexene = 80 mmol/L, NBR latex/MCB = 12.5 (vol./vol.), T = 100 ℃, P_{H_2} =1000 psig

Meanwhile, the hydrogenation conversion plots in the tandem metathesis hydrogenation processes (with or without chain transfer agent) were different from that in the direct hydrogenation process. No induction period was observed.

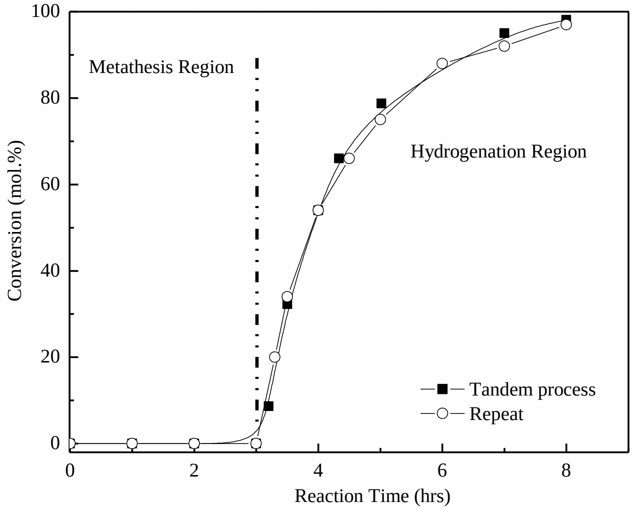


Figure 6-4 NBR latex tandem metathesis hydrogenation under G2 catalyst

Tandem process: commercial NBR latex (50 g/L), total volume = 100 mL, G2 = 0.287 mmol/L, 1-hexene = 80 mmol/L, NBR latex/MCB = 12.5 (vol./vol.), T = 100 ℃, P_{H_2} =1000 psig

6.3.4 Multiple reactions in NBR latex hydrogenation under G2 catalyst

Therefore, combining the molecular weight results for the metathesis reaction with the hydrogenation curve in the tandem metathesis hydrogenation reaction, we could explain the former results (S shape curve and molecular weight change) in the NBR latex metathesis/hydrogenation under the G2 catalyst. When using the G2 catalyst in NBR latex hydrogenation, both the hydrogenation and the metathesis reaction are running in parallel. The reaction can be roughly divided into two regions during the NBR latex hydrogenation. In the first region, although it is very short, the competition between the metathesis reaction and the hydrogenation reaction simultaneously occurs. The existence of metathesis reaction affected the hydrogenation reaction. As a result, the hydrogenation conversion increased slowly and the molecular weight change was mainly affected by the metathesis reaction (molecular weight decreasing process). However, with the presence of H_2 gas under high temperature, the C=Cs in the CTA were quickly reduced. As a result, the cross-metathesis between NBR and CTA is greatly decreased. Although it was reported that metathetic degradation reaction occurred via the inter chain self-metathesis between terminal olefinic structure and vinyl structure [119], this reaction is limited due to the small amount of vinyl structure in commercial NBR (less than 5% in total C=Cs).

In consequence, the metathesis reaction slowed down quickly and hydrogenation reaction dominated the reaction. The molecular weight was mostly affected by the hydrogenation (molecular weight increasing process). Similar phenomena were observed in the NBR solution hydrogenation reaction and natural rubber latex hydrogenation under the G2 catalyst [120, 121].

6.3.5 FT-IR analysis of NBR hydrogenation

Figure 6-5 depicts the FT-IR spectrum of HNBRs using the G2 catalyst at different conversions. During the hydrogenation reaction, the intensity of the peaks representing the unsaturated C=C double bonds were considerably diminished. Similar to the rhodium based catalysts, the G2 catalyst exhibited excellent chemo-selectivity for NBR hydrogenation. The hydrogenation was completely towards the C=C bonds while no nitrile group reductions were observed. Dixneuf et al. studied the tandem cross-metathesis/hydrogenation of fatty esters with acrylonitrile using G2 catalyst [117]. The hydrogenation reaction was completely towards the C=C bonds and nitrile group was intact during the hydrogenation.

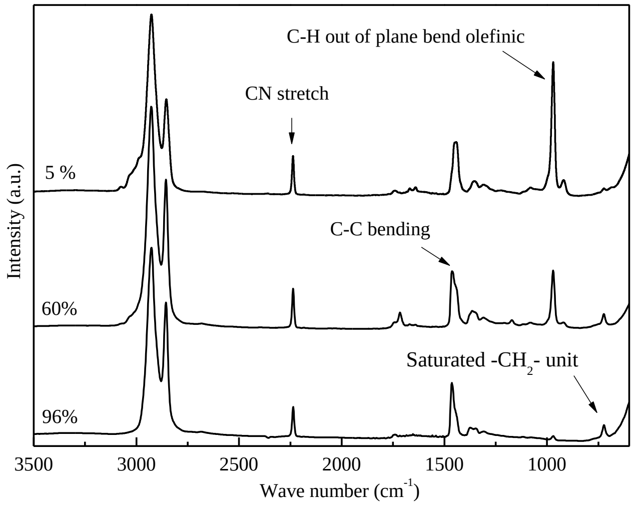


Figure 6-5 FT-IR spectra of the NBR latex hydrogenation with different conversions under G2 catalyst

Commercial NBR latex (50 g/L), total volume = 100 mL, G2 = 0.287 mmol/L, 1-hexene = 80 mmol/L, NBR latex/MCB = 12.5 (vol./vol.), T = 100 ℃, P_{H_2} =1000 psig

6.3.6 The effect of MCB to NBR latex volume ratio on NBR latex metathesis/hydrogenation under G2 catalyst

G2 catalyst could be used in NBR latex hydrogenation with the addition of small volume of MCB. Although the amount of MCB is much less than the previous NBR latex hydrogenation under Ru catalyst, it still increases the separation cost. Therefore, it is very important to control the amount of MCB used in the reaction. Different volume ratios of NBR latex to MCB were studied in the following experiments (Figure 6-6). It was interesting to see that the hydrogenation was even faster when using less amount of MCB (NBR latex to MCB = 50:1 volume ratio). This probably could be explained in that a large amount of MCB could improve the efficiency of the metathesis reaction which further extended the first region of the reaction during the metathesis/hydrogenation. Therefore, the two regions character in the hydrogenation conversion plot is not so evident. In addition, an experiment using the solid G2 catalyst was also tested for NBR latex hydrogenation. As expected, since G2 catalyst couldn't be dispersed homogeneously in the latex system, less than 10 mol.% conversion was observed.

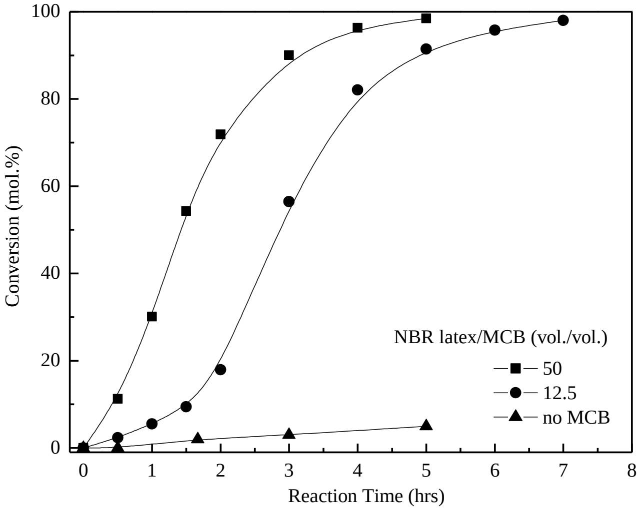


Figure 6-6 The effect of MCB to NBR latex ratio on NBR latex hydrogenation under G2 catalyst

Commercial NBR latex (50 g/L), total volume = 100 mL, G2 = 0.287 mmol/L, 1-hexene = 80 mmol/L, T = 100 ℃, P_{H_2} =1000 psig

6.3.7 Kinetic study of NBR latex hydrogenation under G2 catalyst

Because of concurrent metathesis and hydrogenation reactions, the postulation of the whole reaction pathway seems to be quite complicated. However, it is still worthwhile obtaining the kinetic data for the hydrogenation using G2 catalyst.

To minimize the influence of metathesis reaction, no CTA was added in the following kinetic study experiments. Catalyst solution was also pre-mixed with NBR latex in order to make sure the rare of catalyst diffusion process is minimized. In addition, NBR latex to MCB volume ratio was also kept at constant in all of the experiments. During the reaction, samples were withdrawn from the reaction mixture by a dip tube at pre-determined time intervals and total removed sample is less than 10 vol.% of total NBR volume.

The influences of catalyst concentration, rubber concentration (represented by C=C concentration), hydrogen pressure and reaction temperature on the rate of hydrogenation are summarized in Table 6-2.

Table 6-1 Basic reaction condition and ranges of process variables

Process variable	Basic reaction condition	Experimental Ranges
Pressure of H_2 (psig)	1000	200-1200
Reaction Time (mins)	30	0-300
Stirring Speed (rpm)	600	200-1000
Temperature (°C)	120	90-130
[C=C]/catalyst ratio (mol/mol)	5812	2300-23000

Total volume = 200 mL, NBR latex/MCB = 50:1 (vol./vol.)

Table 6-2 Kinetic experimental data using G2 catalyst

Entry	[Catalyst] (μM)	[C=C] (M)	P (psig)	Temp. ℃	Rate constant k’(×10^3) s^{-1}
1	64	0.93	1000	120	0.567
2	80	0.93	1000	120	0.640
3	80	0.93	1000	120	0.622
4	104	0.93	1000	120	0.783
5	104	0.93	1000	120	0.791
6	128	0.93	1000	120	0.842
7	128	0.93	1000	120	0.861
8	160	0.93	1000	120	1.233
9	160	0.93	1000	120	1.250
10	240	0.93	1000	120	1.820
11	160	0.37	1000	120	2.342
12	160	1.86	1000	120	1.039
13	160	2.79	1000	120	0.868
14	160	3.72	1000	120	0.628
15	160	0.93	600	120	0.455
16	160	0.93	700	120	0.626
17	160	0.93	800	120	0.847
18	160	0.93	900	120	1.092
19	160	0.93	1100	120	1.291
20	160	0.93	1200	120	1.299
21	160	0.93	1200	80	0.153
22	160	0.93	1000	90	0.232
23	160	0.93	1000	100	0.420
24	160	0.93	1000	110	0.730
25	160	0.93	1000	110	0.721
26	160	0.93	1000	120	1.284
27	160	0.93	1000	130	1.879

The system under study is a multiphase system, consisting of hydrogen gas, an aqueous phase and a solid with catalyst and substrate. In such a reactive system, the overall conversion rate may be limited by, among other things, gas-liquid mass transfer of hydrogen gas and transfer of catalyst between liquid and solid phases. For determination of the intrinsic kinetics, it is advantageous to perform the experiments in the chemically controlled kinetic regime. To gain insights in possible mass transfer effects, some experiments were performed at different agitation rates while keeping all other variables at basic conditions (Table 6-1). The conversion of NBR for a 30 minutes reaction time as a function of the stirring speed is given in Figure 6-7. The HNBR conversion level is clearly a function of the agitation rate when the agitation rate is below 800 rpm. This implies that the reactions below 800 rpm are affected by mass transfer effects. Above 800 rpm, the HNBR is essentially independent of the stirring rate, an indication that these experiments were performed in the kinetic regime. Therefore, the following experiments were performed at agitation rate of 800 rpm to ensure the hydrogenation reactions take place in the kinetic region.

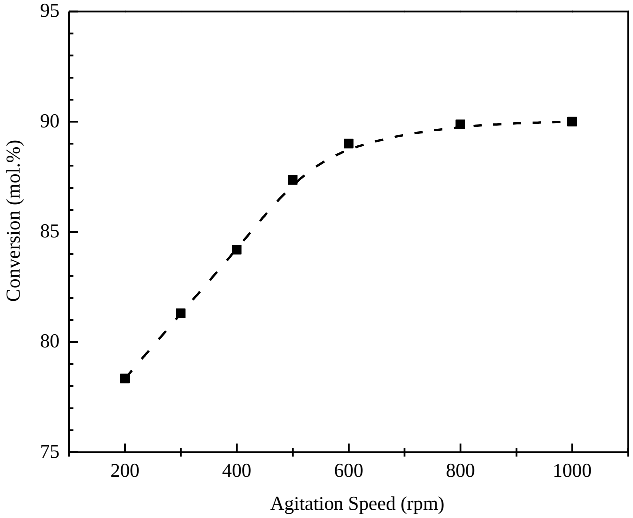


Figure 6-7 Conversion of NBR at various agitation rates after 30 minutes

(All other variables are at base conditions, Table 6-1)

The hydrogenation reaction was studied in the range of 80 ℃ and 130 ℃ (Figure 6-8). It is clear that the temperature plays a very important role in the hydrogenation reaction. The reaction time (reach 95 mol.% conversion) greatly shortened with the increase in temperature. The initial reaction rate is highest at the highest temperature in the range.

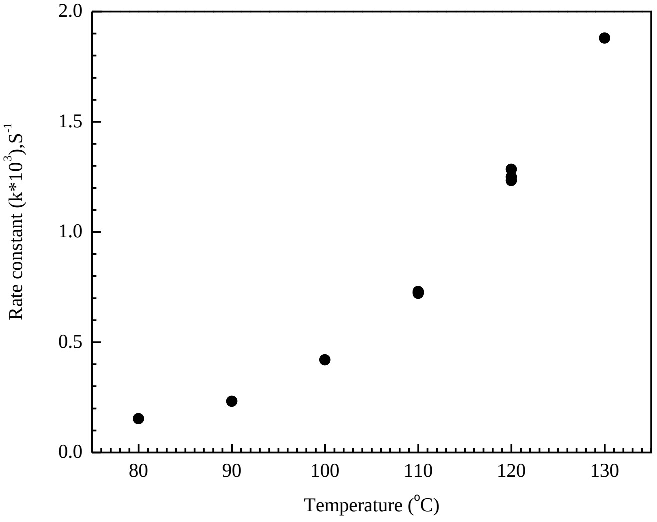


Figure 6-8 Effect of temperature on rate of NBR hydrogenation

(All other variables are at base conditions, Table 6-1)

The effect of the initial NBR concentration on the reaction rate was determined at a fixed catalyst intake. The concentrations were investigated over the range of 0.372~3.72 mol/L and is presented in Figure 6-9. The rate of reaction decreased with an increase in rubber concentration. The inhibiting effect of nitrile unsaturation on the NBR hydrogenation reaction rate has been observed by Parent et al. [95] and Mohammadi et al. [96] respectively. At the temperature and pressures used in this work, identifying the influential modes of nitrile complexation is difficult. However, the FT-IR results suggest that although nitrile coordinates to species involved in olefin hydrogenation, it is not reduced concurrently.

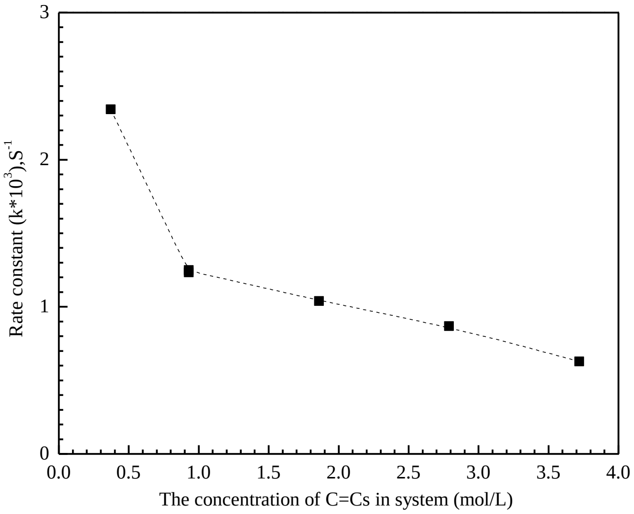


Figure 6-9 Effect of rubber concentration on rate of hydrogenation of NBR latex

(All other variables are at base conditions, Table 6-1)

The effect of catalyst concentration on the initial NBR reaction rate was studied by performing experiments with a variable catalyst intake at a fixed initial NBR intake at basic conditions. The experimental results, as shown in Figure 6-10, suggest that the hydrogenation reaction is first order in catalyst for this hydrogenation system.

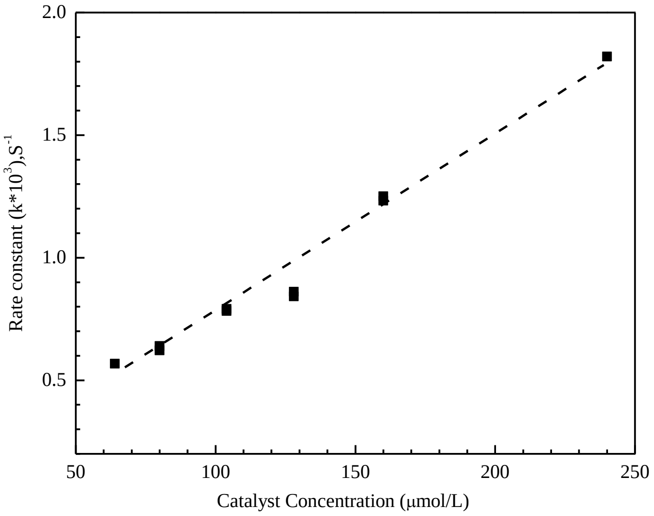


Figure 6-10 Effect of catalyst concentration on rate of hydrogenation of NBR latex

(All other variables are at base conditions, Table 6-1)

Eight experiments with hydrogen pressures ranging from 600 to 1200 psig were performed at basic conditions to determine the effect of hydrogen on the initial reaction rate of NBR. The results are given in Figure 6-11. The figure indicates that the initial reaction rate of NBR is independent of the hydrogen pressure when the pressure exceeds 1000 psig. At lower pressures, a first order dependency is observed.

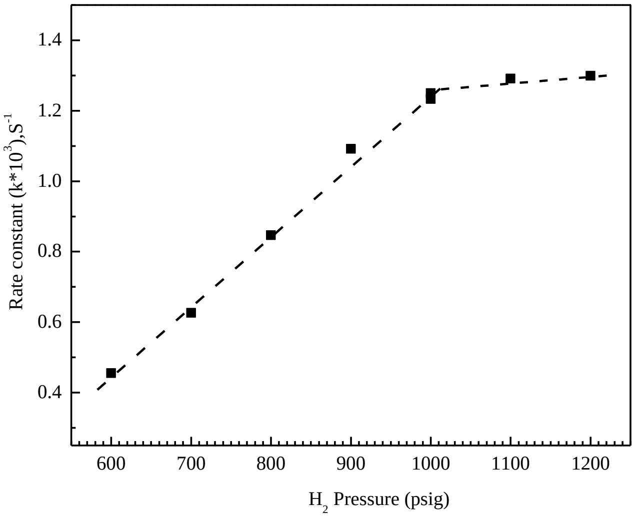


Figure 6-11 Effect of hydrogen pressure on rate of hydrogenation of NBR latex

(All other variables are at base conditions, Table 6-1)

The Arrhenius plot provided in Figure 6-12 illustrates the influence of temperature on the rate of hydrogenation. Over the range of 80-130 ℃, a linear response is observed, from which apparent activation energies of 74.9 kJ/mol is derived. This estimate shows that the experiments were carried out without mass transfer limitation; else the reaction rates would be relatively insensitive to temperature variations.

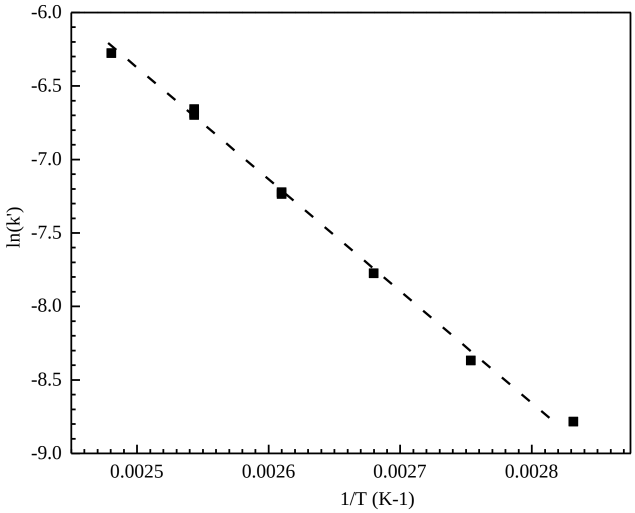


Figure 6-12 Arrhenius plot for the hydrogenation of NBR

(All variables are at base conditions, Table 6-1)

6.4 Summary

Grubbs 2^{nd} generation catalyst (G2) was investigated for NBR latex hydrogenation. The insoluble G2 catalyst could not be dispersed in the NBR latex and a low conversion (< 20 mol.%) was obtained by directly using the solid catalyst. With the addition of organic solvent, NBR latex could be successfully hydrogenated to a high conversion in the presence of G2 catalyst.

When conventional ruthenium based hydrogenation catalysts were used for NBR hydrogenation (solvent, latex or bulk), one of the main problems was the gel formation. A very significant finding here was that the hydrogenated NBR under G2 catalyst was completely soluble in organic solvent and no visible gel formation was observed. In addition, we could still observe that the molecular weight increased during the hydrogenation, the molecular weight reduction from the metathesis reaction offsets, or at least partly offsets the cross-linking effect during hydrogenation. In addition, we also observed that extension of metathesis is limited in the latex system under a mixed metathesis/hydrogenation reaction process.

Finally, this is the first time to find that Grubbs 2nd generation catalyst was active for NBR latex hydrogenation in the presence of a very limited amount of required organic solvent which is used for dissolving the catalyst. Under the suitable reaction conditions, the hydrogenation could be completed within a few hours, which is much faster than that observed with rhodium based catalyst.

Chapter 7

NBR latex hydrogenation with second generation of Hoveyda-Grubbs catalyst

Inspired by the promising finds on NBR latex hydrogenation using second generation of Grubbs catalysts (G2), other Grubbs type catalysts were tested for NBR latex hydrogenation. Among the catalysts, we found second generation of Hoveyda-Grubbs catalyst (HG2) is also effective for NBR latex hydrogenation. More importantly, the reaction could be performed without adding any organic solvents to dissolve the HG2. The experimental results are presented in this chapter.

7.1 Introduction

Based on our findings in the chapter before, Ruthenium carbene complexes such as second generation of Grubbs generation catalyst could be used for NBR latex metathesis/hydrogenation. Among the Grubbs type catalysts, Grubbs 1st (G1), Grubbs 2nd (G2), Hoveyda-Grubbs 1st (HG1) and Hoveyda-Grubbs 2nd (HG2) generation catalysts are readily available and have widely used as metathesis catalysts for different reactions. Since most of Grubbs type catalysts are insoluble in water, the use of catalysts in an aqueous system largely remain the domain of catalyst design. However, the allure of aqueous olefin metathesis also requires developing suitable aqueous reaction conditions for the available Grubbs type catalysts [122-124].

In the initial work with well defined catalysts in aqueous systems, Grubbs and co-workers performed ring-opening metathesis polymerization (ROMP) with G1 catalyst in aqueous emulsions [125, 126]. Piland et al. used G1 and G2 catalysts for the metathetic degradation of polyisoprene in both an organic solvent and in an aqueous latex phase [127]. It was found that the G2 catalyst is active in the aqueous phase only with the addition of acetonitrile as a co-solvent to dissolve the catalyst. Raines et al. examined the performance of different conventional Grubbs catalysts in homogeneous water/organic mixtures, finding that the HG2 exhibited high conversions (71-95 mol.%) in aqueous dimethoxyethane and aqueous acetone system for both ring close metathesis and cross metathesis [128]. Most recently, Mingotaud et al. discovered that HG2 catalyst in micellar solutions of ammonium surfactants (e.g. DTAC and CTAC) showed the potentiality of ring-opening metathesis polymerization with a hydrophilic monomer [129].

As we know, NBR latex is also an aqueous micellar system with hydrophobic substrates in the micelles. It is very similar to the reaction system which Mingotaud et al. used in their research. Therefore, the activity of HG2 catalyst for the NBR latex hydrogenation was examined. Different from using G2 catalyst where we dissolved the catalyst in organic solvent, we found solid HG2 catalyst could be used for NBR latex hydrogenation without adding any organic co-solvent.

7.2 Experimental

7.2.1 Organic solvent free NBR in latex hydrogenation under HG2 catalyst

The hydrogenation reaction was carried out in a 300 mL Parr reactor. 100 mL NBR latex (if not otherwise specified) was added to the reactor. The solid HG2 catalyst weighed in a small glass bucket and then was placed in a catalyst addition device which is installed in the head of the reactor. After assembling the reactor, the NBR latex was degassed by bubbling nitrogen gas under about 200 psig for 20 min at room temperature and the system was heated to the desired reaction temperature. Then, the system was stabilized for 30 minutes and the catalyst was added into the NBR latex with hydrogen gas. The hydrogen pressure and reaction temperature were kept constant throughout the reaction period. The hydrogenated NBR latex was sampled through a dip tube at intervals during the reaction.

7.2.2 Organic solvent free metathesis of NBR with co-olefins in NBR latex with HG2

The metathesis reaction was carried out in the same reactor. After degassing the NBR latex, change transfer agent (CTA) was added and the temperature was changed to the reaction temperature. Then the solid catalyst was added to the NBR latex under N_2. The structure and the molecular weight of polymer products were measured by FT-IR and GPC.

7.2.3 Characterization

The solubility of the HG2 catalyst in the aqueous system was measured by UV-Vis. The hydrogenation degree was measured by FT-IR. The molecular weight of NBR and the resultant HNBRs were measured by GPC. The metal concentration in polymer particles was measured by ICP-OES. The morphology of the NBR latex was measured by DLS and TEM. Detailed characterization procedures have already been provided in Chapter 3.

7.3 Results and discussion

7.3.1 The solubility of HG2 in water and water/surfactant system

To demonstrate that HG2 catalyst can be dispersed in an aqueous micellar phase, two types of surfactant were used: cationic surfactant dodecyltrimethylammonium chloride (DTAC) and anionic surfactant sodium dodecyl sulfate (SDS). First, the UV–visible absorbance spectrum of DTAC surfactant solution in contact with HG2 in a solid form was examined. As shown in Figure 7-1, almost no absorbance for the HG2 catalyst in the case of pure water. When surfactant DTAC was added, the band at about 380 nm gradually appeared. This band is very similar to the ones of HG2 catalyst dissolved in methylene chloride (see Figure 7-2) and therefore could be associated to the dispersed HG2 catalyst. It was also observed that the absorbance intensity increased when more surfactant added (curve b-e).

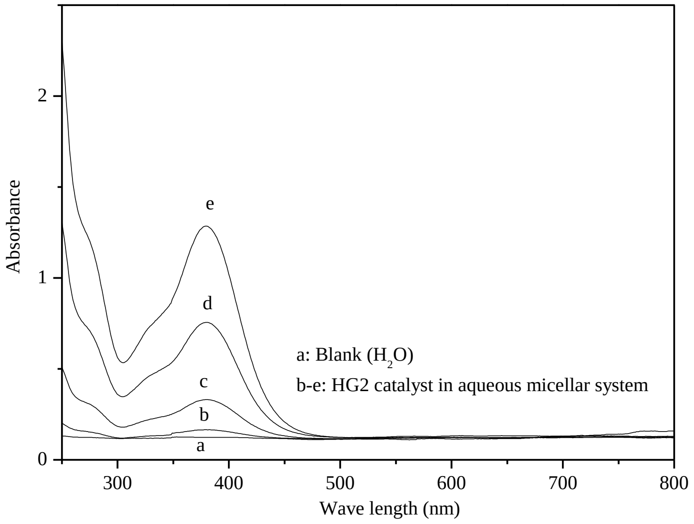


Figure 7-1 UV-vis spectrum of HG2 catalyst in water with different amounts of DTAC surfactant

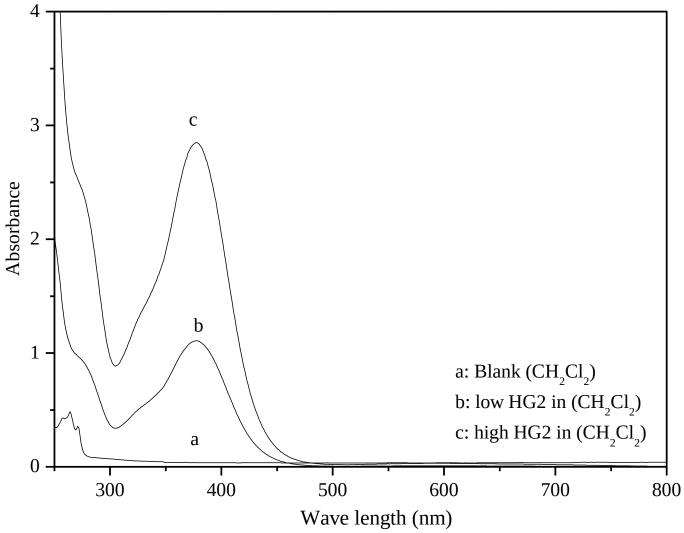


Figure 7-2 UV-vis spectrum of HG2 catalyst in CH_2Cl_2 solution

The solubility of HG2 catalyst in anionic surfactant (SDS) was measured under the same way as that in cationic surfactant. Due to the UV adsorption of SDS, the distinct peak for HG2 was overlapped in the UV-vis spectrum. However, under a high surfactant concentration, we still could be a small shoulder peak at 380 nm (Figure 7-3), indicating HG2 catalyst still could be dispersed in the aqueous system with anionic surfactant.

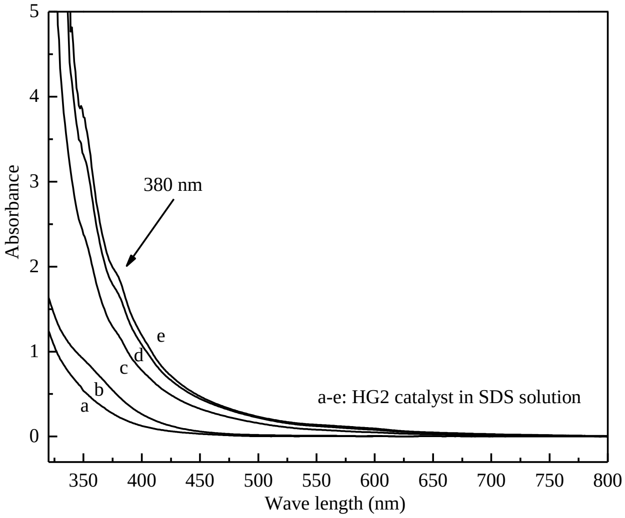


Figure 7-3 UV-vis spectrum of HG2 catalyst in water with different amount of SDS surfactant

For comparison, the solubility of G2 catalyst in aqueous micellar system was also examined. Figure 7-4 depicts the UV-Vis spectroscopy of G2 catalyst dissolved in methylene chloride and Figure 7-5 shows the results in aqueous system. A very distinctive peak at 330 nm was found in Figure 7-4. However, this peak couldn’t be observed when G2 catalyst mixed with water. This means the solubility of G2 catalyst in aqueous micellar was substantially limited. This result also confirms we findings in chapter 6 that high conversions could not be achieved using G2 catalyst without the addition of MCB.

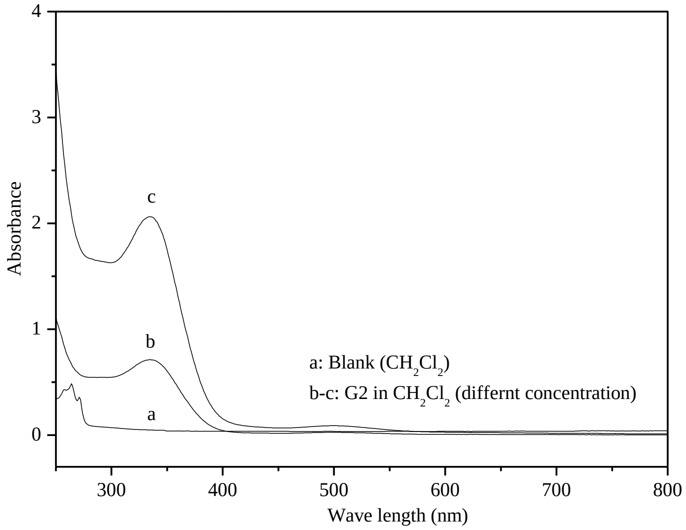


Figure 7-4 UV-vis spectrum of G2 catalyst in CH_2Cl_2 solution

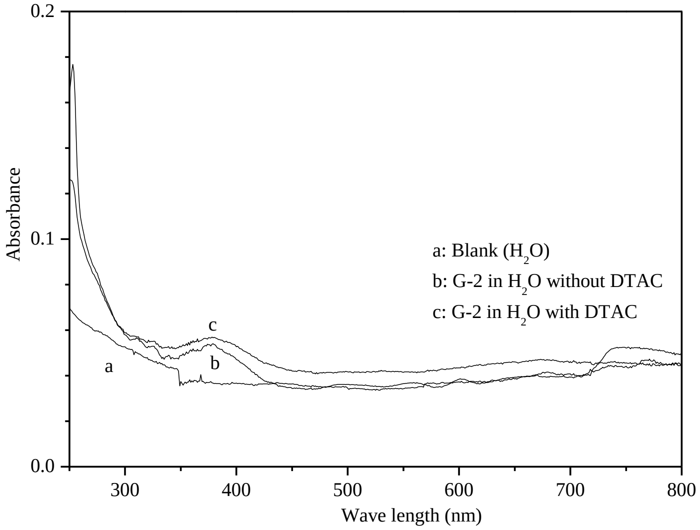


Figure 7-5 UV-vis spectrum of G2 catalyst in water with different amount of DTAC surfactant

7.3.2 Organic solvent free NBR latex hydrogenation under HG-2 catalyst

Representative experiments with operational conditions and final conversions of NBR latex hydrogenation by HG2 under different catalyst loadings (10~310 μmol/L), reaction temperature (100 and 120 ℃) and H_2 pressure (500, 1000 and 1500 psi) are listed in Table 7-1.

The catalyst loading (shown as HG2 in Table 7-1) has an interesting effect on the hydrogenation rate and the conversion. With a low catalyst loading, such as in entry 1 and 2, where the concentration is 10 μmol/L and 2 μmol/L, respectively, the C=C bonds cannot be completely hydrogenated (the reaction in Entry 1 and 2 terminated at the time shown and any further extension of the operational time did not result in further conversion.). With the increase of the catalyst amount, the extent of the reaction is significantly improved and high conversions could be achieved (entry 3 - entry 6). However, the data in Table 1 also indicated that once the catalyst amount used exceeded a certain level, part of the catalyst may not contribute to the reaction, as shown by comparing entry 4, 5 and 6. When the catalyst concentration increased from 78 μmol/L to 156 μmol/L, the reaction time shortened from 1.6 hours to 0.5 hour. When further increase the catalyst concentration to 310 μmol/L, the reaction time only dropped to 0.4 hour. Similar results of the reaction time were also observed at the low temperature using different catalyst concentration (entry 8 - entry 10). This is because when the HG2 amount reaches a certain level, some of the catalyst may not be diffused into the micelles. Instead, it remains in clusters suspended in the water phase or settles out of the water phase and does not contribute effectively to the reaction.

The effect of reaction temperature and pressure on the extent of hydrogenation conversion can also be observed from the results in Table 7-1. The hydrogenation reaction was studied at 100 ℃ and 120 ℃ at a constant reaction pressure of 1000 psi and 78 μmol/L of catalyst (entry 4 & 9). It is clear that the temperature plays a very important role in the hydrogenation reaction. The reaction time (at same final conversion) greatly decreased from 4 hours to 1.6 hours with the increase in temperature. The effect of the H_2 pressure was compared under different temperatures. It was found that the reaction rate was significantly affected under the lower pressure range (entry 9 at 1000 psi & entry 11 at 500 psi) while this affection was not so evident at higher pressure range (entry 3 at 1000 psi & entry 7 at 1500 psi). Finally, the original NBR latex (no dilution with DI water) was tested (entry 12) and completely hydrogenation was observed from the result.

Table 7-1 Hydrogenation of NBR in latex under HG2 catalyst (no co-olefins) [a]

Entry	**HG2** (µmol/L)	**T** (℃)	**P_{H2}** (psig)	**Time** (hrs)	**Conversion**[b] (mol.%)	**TOF**[c] (h^{-1})
1	10	120	1000	15	50	-
2	20	120	1000	10	74	-
3	39	120	1000	10.5	95	1333
4	78	120	1000	1.6	98	4514
5	156	120	1000	0.5	99	7222
6	310	120	1000	0.4	99	4542
7	39	120	1500	9.0	95	1558
8	39	100	1000	19	90	-
9	78	100	1000	4	98	1810
10	39	100	1000	1	99	1444
11	78	100	500	10	99	722
12[d]	200	100	1000	3	99	4827

a. Commercial NBR latex (50 g/L);

b. Conversions determined by FT-IR;

c. Defined as mole of hydrogenated C=C units in the NBR per mole of HG2 catalyst added per hour (based on 95 mol.% conversion);

d. 100mL original NBR latex (200 g/L).

7.3.3 Characterization

7.3.3.1 FT-IR analysis

Figure 7-6 depicts the FT-IR spectral of NBR latex hydrogenation using HG2 with different conversions. During the hydrogenation reaction, the intensity of peaks at 970 cm^{-1} and 920 cm^{-1} diminished considerably while the peak at 723 cm^{-1} appeared. Superior selectivity was also observed under the HG-2 catalyst. No characteristic signals for primary (two bands from 3250 cm^{-1} to 3400 cm^{-1}) or secondary amines (one band from 3310 to 3350 cm^{-1}) were found in the FT-IR spectra, indicating that the hydrogenation was selective towards the C=C bonds.

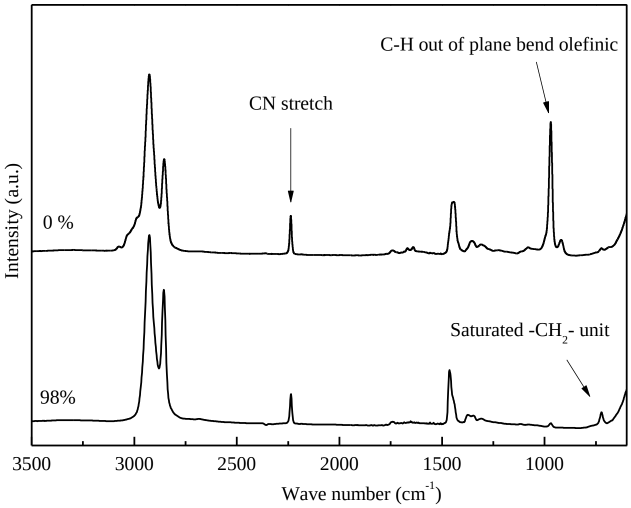


Figure 7-6 FT-IR spectra of the NBR latex hydrogenation with different conversions under HG2 catalyst

Commercial NBR latex (50 g/L), total volume = 100 mL, HG2 = 78 µmol/L, Temperature = 100 °C, P_{H_2} = 1000 psig

7.3.3.2 Morphology of NBR latex during the hydrogenation

We next turned our attention to the morphology of the NBR/HNBR latex. During hydrogenation operations, no coagulation of the latex was observed. The average particle sizes of the latex before and after hydrogenation remained almost unchanged (as shown in **Error! Reference ource not found.**), which means hydrogenation had no adverse effect on the latex particle size or stability.

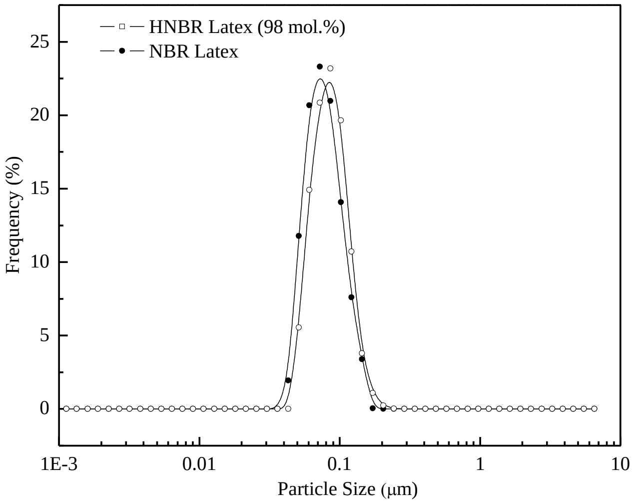
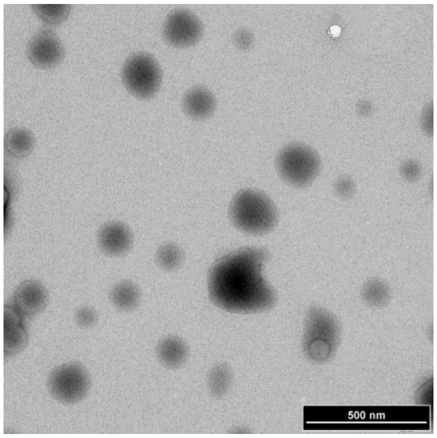


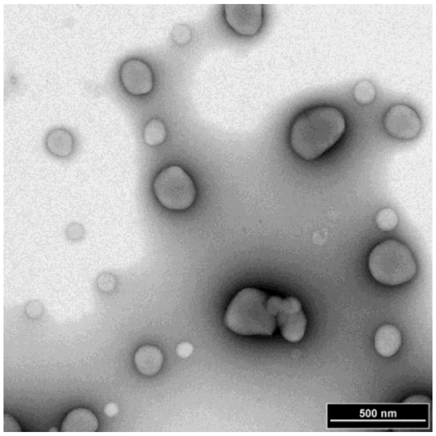
Figure 7-7 Particle size distributions in the lattices before/after hydrogenation

Commercial NBR latex (50 g/L), total volume = 100 mL, HG2 = 78 μmol/L, T = 100 ℃, P_{H_2} = 1000 psig

Figure 7-8 showed TEM micrographs of NBR latex before/after hydrogenation step. Since the staining agent can only stain double bonds, lightly color domains should indicate lower double-bond concentrations. For comparison, NBR latex (without hydrogenation, particle size 80 nm) (A) and the HNBR latex with a 99 mol.% conversion (B) are also depicted. The non-hydrogenated NBR (A) shows relatively dark because the concentration of the staining agent inside the particle is high. On the other hand, the hydrogenated HNBR latex (B) exhibits a much lighter color due to the few amounts of the double bonds available for staining.



(A)



(B)

Figure 7-8 TEM micrographs of (A) non-hydrogenated NBR latex; (B) completely hydrogenated NBR latex

Commercial NBR latex (50 g/L), total volume = 100 mL, HG2 = 78 μmol/L, T = 100 ℃, P_{H_2} = 1000 psig

7.3.3.3 The position of the catalyst in NBR latex during hydrogenation

When using HG2 catalyst, no co-catalyst ligand or organic co-solvent was added. Therefore, the diffusion of the catalyst from the aqueous phase into the NBR particles has to be achieved by catalyst itself. The UV-vis analytical results have showed that catalyst could be separated in the aqueous system with the addition of selected surfactants. Here, the Ru metal (from HG2 catalyst) concentration inside the polymer particles was also quantitatively measured by ICP-OES.

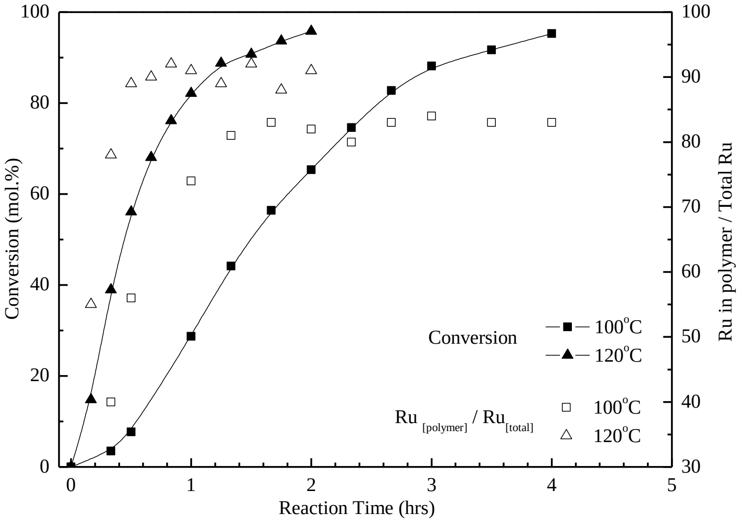


Figure 7-9 Ruthenium (from HG2 catalyst) concentration in polymer particles during the hydrogenation

Commercial NBR latex (50 g/L), total volume = 100 mL, HG2 = 78 μmol/L,
Temperature = 100 ℃, P_{H_2} = 1000 psig

The percentage of catalyst in polymer during the hydrogenation reaction (conversion vs time) is shown in Figure 7-9. Comparing the metal in polymer particles to the metal original added, it was found that a large proportion of catalyst was transferred into the polymer particles. A small induction period was observed at 100 ℃ due to the catalyst diffusion process. The catalyst concentration in polymer particles quickly increased during the reaction and reached the equilibrium.

7.3.4 Metathesis in NBR latex without organic co-solvent

The metathesis reaction by HG2 catalyst with different kinds of co-olefins was investigated in aqueous NBR latex system. Still no organic co-solvent was used. The results of the molecular weight of polymer product are summarized in Table 7-2. It was found when using propylene and 1, 3-butadiene as co-olefin the molecular weight of the polymer product was almost the same as the original NBR. This is because both of them cannot dissolve NBR or catalyst and no metathesis occurred. Although the cross-metathesis (CM) of electron-deficient substrates such as acrylonitrile with terminal alkenes was problematic with the phosphine-containing catalyst (e.g. Grubbs 2nd catalyst), it was reported the HG2 catalyst could promote such reaction in high yield [130]. However, using acrylonitrile as CTA, no evident molecular weight decrease was observed by GPC analysis. The constant nitrile group (≡CN) concentration in the final product also confirms the absence of metathesis reaction. Finally, styrene was used as a co-olefin. After 8 hours, the molecular weight of the product greatly reduced. The GPC results showed a molecular weight decrease of 1 order of magnitude along with the generation of a most probable polydispersity (PDI = 2.0), indicates that metathesis depolymerization equilibrium has been reached. This is because styrene can not only provide C=C as an olefin, but also it can works as an efficient solvent to dissolve both the HG2 catalyst and NBR polymer, and so makes a more uniform reaction system. The new peaks at 970 and 700 cm^{-1}, representing the phenyl ring in the styrene, also confirm the metathesis reaction between NBR and styrene (Figure 7-10). Besides, the introducing benzyl group via cross-metathesis opens a new route to produce acrylonitrile-butadiene polymer with embedded styrene functional group which might expand the application of original NBR.

Table 7-2 Metathesis of NBR in latex with different co-olefins under HG2 catalyst

Entry	Reaction Time	Co-olefin^2	Molecular Weight		
			Mn	Mw	PDI
1(NBR)	-	-	68,751	206,448	3.00
2	10	Propylene^3	67,944	198,131	2.91
3	8	1,3-butadiene^4	66,929	195,812	3.03
4	10	acrylonitrile	72,000	211,540	2.95
5	8	styrene	16,271	31,750	1.95

^{1} $[C=C]_{NBR}$: [Catalyst] = 3500:1; ^{2} $[C=C]_{NBR}$: [co-olefin] = 20:1; ^{3} $P_{propylene}$ = 150 psig; ^{4}T= 20 ℃

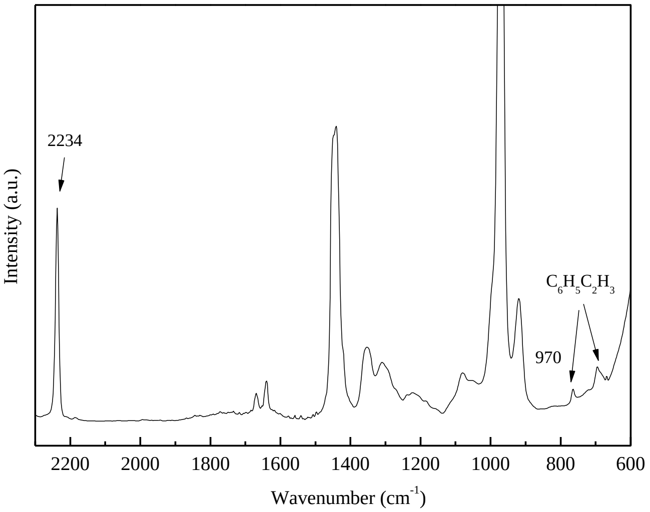


Figure 7-10 Metathesis of NBR with styrene (CTA) in NBR latex

Reaction conditions are listed in Table 7-2

7.4 Conclusions

Here, we find that with the well-defined Hoveyda-Grubbs' second generation catalyst (HG2), hydrogenation of NBR latex could be successfully achieved without any added organic solvent. The analysis results show that the C=C double bonds in NBR polymer chain can be completely hydrogenated under suitable experimental conditions. The hydrogenation reaction for the direct hydrogenation of the NBR latex under HG2 is still faster than that observed with rhodium based catalysts and is comparative to the commercial solution process, which implies that conventional hydrogenation processes can be significantly 'greened' by eliminating the use of such a large amounts of organic solvents, and that pre-treatment and post-treatment operations can be significantly simplified. Meanwhile, metathesis reaction was observed when adding suitable small co-olefins such as styrene and resultant polymer product has a smaller molecular weight than the original NBR.

Chapter 8

Conclusions and Recommendations for Future Research

8.1 Conclusions

8.1.1 Comparison of catalysts for NBR latex hydrogenation

All of the catalysts developed and used in this research are listed below in Table 8-1.

Table 8-1 Comparison of different catalysts for latex hydrogenation

Catalysts	Ligand	Solvent	Max. Conversion	Gel
$RhCl(PPh)_3$	PPh_3	-	~95	No
$RhCl_3$	PPh_3	-	~95	Micro-gel
$RhCl_3$	PPh_3	Ethanol	~95	No
$RhCl(TPPMS)_3$	-	-	~95	No
$RhCl(TPPTS)_3$	-	-	~30	gel
G2	-	MCB	~99	No
HG2	-	-	~99	No

The activities are not directly compared with each other because experimental conditions such as catalyst loading, reaction temperature, the addition of co-catalyst ligand or co-solvent are different from each other.

It can be seen that a series of rhodium and ruthenium based catalysts are suitable for the hydrogenation of NBR in latex form. For the $RhCl(PPh_3)_3$ catalyst, the presence of triphenylphosphine is crucial for obtaining a desired conversion. It facilitates the transport of the $RhCl(PPh_3)_3$ catalyst from the aqueous phase into the polymer particles.

Based on the catalyst diffusion requirement, the in-situ synthesized $RhCl(PPh_3)_3$ catalyst from water-soluble catalyst precursor $RhCl_3$ and PPh_3 was developed. Since $RhCl_3$ could be dissolved in the aqueous phase in the NBR latex, the transportation of the in-situ synthesized catalyst was quicker than pre-made solid catalyst. However, it was also found the in-situ synthesis efficiency is still limited due to the low solubility of triphenylphosphine in water. As a result, the un-reacted $RhCl_3$ triggered a cross-linking side reaction which affected the viscosity of HNBR. To solve this problem, a small amount of alcohol was introduced into the reaction system. With the addition of alcohol, the in-situ synthesis efficiency greatly improved. Compare with previous in-situ method, the in-situ synthesis efficiency was improved and the hydrogenation reaction rate was increased. Not only that, the cross-linking side reaction is also alleviated.

With the success of using $RhCl(PPh_3)_3/PPh_3$ catalytic system for NBR latex hydrogenation, two water-soluble analogs of $RhCl(PPh_3)_3$, $RhCl(TPPMS)_3$ and $RhCl(TPPTS)_3$ were tested for NBR latex hydrogenation. These catalysts have been studied for NBR latex hydrogenation before and no industrially required conversion was reported. However, under our reaction condition, we found that the required conversion could be achieved using the $RhCl(TPPMS)_3$ catalyst. Different from $RhCl(PPh_3)_3$ catalyst, co-catalyst ligand were not required when using $RhCl(TPPMS)_3$. When using the $RhCl(TPPTS)_3$, the catalyst remained in the aqueous phase and only low conversion was observed at the end of reaction. The result of Rh concentration within the polymer particles confirmed the hydrogenation result by showing very low amount of catalyst in the polymer particles.

With the new discoveries on NBR solution metathesis/hydrogenation using the new ruthenium catalyst (Grubbs type catalysts), the activity of these catalysts for NBR latex was studied for the first time. The Grubbs second generation (G2) catalyst is dissolved in a small amount of MCB and this catalyst solution was used for NBR latex hydrogenation. More than 98 mol.% conversion can be achieved with suitable system compositions. Meanwhile, the previous cross-linking problem exhibited with ruthenium based catalysts was partly offset by the metathesis ability of the G2 catalyst.

We also discovered the superior activity of Hoveyda-Grubbs 2nd generation (HG2) catalyst for the hydrogenation reaction in NBR latex system. Compared with all the other catalysts, the HG2 catalyst showed the overall best performance for NBR hydrogenation in latex form. An exceptional rapid catalytic hydrogenation (TOF > 7000 h^{-1} at 95 mol.% conversion) could be achieved and hydrogenation reaction was still feasible at a very low catalyst concentration. More importantly, no organic solvent and/or co-catalyst are used.

8.1.2 Optimization of the latex hydrogenation system

The optimization of the latex hydrogenation system includes the screening of catalysts and improving the catalyst mass transfer.

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.

8.1.3 Research contributions

As a result of this research project, new latex hydrogenation technologies including highly efficient catalytic systems, suitable reaction operation conditions to improve the hydrogenation rates were successfully developed. Using these technologies, the direct catalytic hydrogenation of NBR latex was realized with a degree of hydrogenation higher than 95 mol.% without visible gel formation. The hydrogenation reaction rate increased and became comparable to the NBR solution hydrogenation process. The new NBR latex hydrogenation process especially under the

$RhCl(TPPMS)_3$ and Hoveyda-Grubbs 2nd catalysts fulfill all major requirements for developing an economical polymer latex hydrogenation route and represents a significant milestone for improvements of the polymer modification technologies.

This research project showed that the catalytic ability of rhodium and ruthenium based catalysts for polymer hydrogenation. With the progress of this research project, more knowledge was accumulated for the scientific field of diene-based polymer modification and some informative results have been reported from our lab for different types of polymer latices.

8.2 Recommendations for future research

There are still many issues require investigation for the development of successful latex hydrogenation processes:

- Understanding the mechanism of the cross-linking reaction triggered by the $RhCl_3$ with suitable technology and characterization methods such as ^{13}C NMR;
- Understanding the relationship between metathesis and hydrogenation using G2 catalyst for NBR latex metathesis/hydrogenation;
- Screening more catalysts for the latex hydrogenation. Based on Gilliom's findings [35] on the bulk hydrogenation of olefinic polymers using Iridium based Crabtree catalyst, Ir based catalyst might be another promising group of catalysts for latex hydrogenation;
- Conducting a systematic kinetic and mechanism study for the latex hydrogenation in order to further optimize the latex hydrogenation.

8.2.1 Future investigation of the catalytic system

8.2.2 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 residue in the resulting polymer. The catalyst separation investigation will be the focus of further latex hydrogenation work.

8.2.3 Exploration of the potential application for other latex systems

Prior to the success realized for solvent-free NBR latex hydrogenation, a polymer hydrogenation process usually included dissolution of polymer, hydrogenation, separation and drying. The extra cost for hydrogenation is always a major factor that inhibits the wide 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.

Both the rhodium and ruthenium based catalysts were found to be excellent catalysts that can be used in the NBR latex hydrogenation system. It is worthy of exploring its application for other latex systems.

Appendix

This research project is a confidential project sponsored by Lanxess Deutschland GmbH.

The original data for all experiments are only provided in the copies which are used internally.

Publications and Patents

1. G.L. Remepl, Q. Pan, Y. Liu, Tandem metathesis and hydrogenation of diene-based polymers in latex (Patent pending, assigned to Lanxess Deutschland GmbH)

2. G.L. Remepl, Q. Pan, Y. Liu, Hydrogenation of diene-based polymers (Patent pending, assigned to Lanxess Deutschland GmbH)

3. G.L. Remepl, Q. Pan, Y. Liu, Hydrogenation of a diene-based polymer latex (Patent pending, assigned to Lanxess Deutschland GmbH)

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