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Homogeneous Catalytic Hydrogenation of Polymers

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19.1

General Introduction

Chemical modification of polymers via catalysis is of great importance as it provides an efficient synthetic route for the production of novel polymers with desirable physical properties. It also allows the introduction of functional groups that are often inaccessible by conventional polymerization techniques. One of the most important chemical modifications is the hydrogenation of unsaturated carbon-carbon double bonds in polymers. Basically, there are two technical routes for the hydrogenation of polymers: homogeneous and heterogeneous. This chapter reviews research and process development with respect to homogeneous catalytic hydrogenation of diene-based polymers.

19.1.1

Diene-Based Polymers

Diene polymers refer to polymers synthesized from monomers that contain two carbon-carbon double bonds (i.e., diene monomers). Butadiene and isoprene are typical diene monomers (see Scheme 19.1). Butadiene monomers can link to each other in three ways to produce *cis*-1,4-polybutadiene, *trans*-1,4-polybutadiene and 1,2-polybutadiene, while isoprene monomers can link to each other in four ways. These dienes are the fundamental monomers which are used to synthesize most synthetic rubbers. Typical diene polymers include polyisoprene, polybutadiene and polychloroprene. Diene-based polymers usually refer to diene polymers as well as to those copolymers of which at least one monomer is a diene. They include various copolymers of diene monomers with other monomers, such as poly(butadiene-styrene) and nitrile butadiene rubbers. Except for natural polyisoprene, which is derived from the sap of the rubber tree, *Hevea brasiliensis*, all other diene-based polymers are prepared synthetically by polymerization methods.



Scheme 19.1 The monomers butadiene and isoprene.

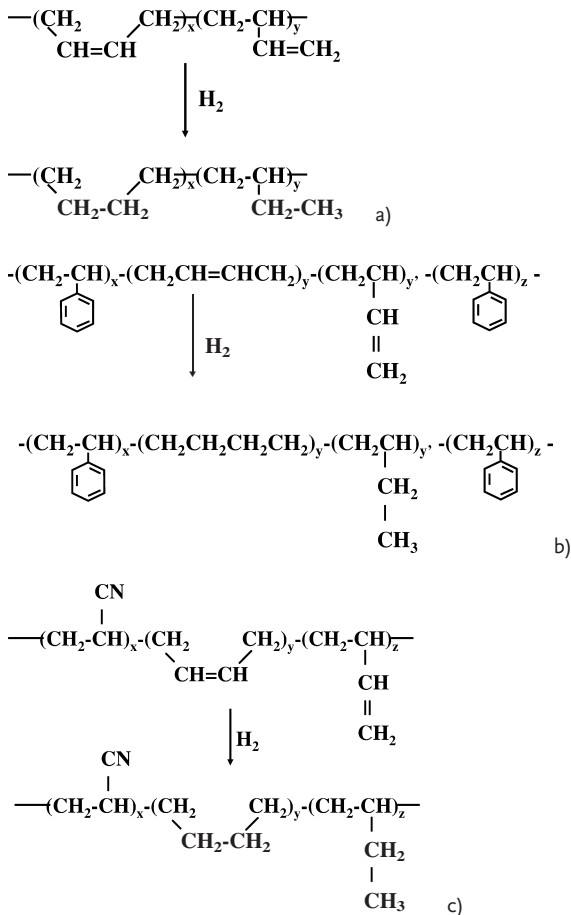
19.1.2

Hydrogenation of Diene-Based Polymers

Polymers obtained by polymerizing or copolymerizing conjugated dienes are widely utilized for commercial purposes. These polymers have residual double bonds in their polymer chains. A limited amount of these residual double bonds are advantageously utilized for vulcanization, yet the residual double bonds have a disadvantage in that they lack the stability to resist weather conditions, oxidation, and ozone. Such disadvantages are more severe for block copolymers of conjugated dienes and vinyl aromatic hydrocarbons when used as thermoplastic elastomers. Moreover, the disadvantages are even more severe when the polymers are used as modifiers and transparent impact-resistant materials for styrenic resins and olefinic resins, or when they are used to make parts of equipment for utilization in solvent/oily/high-temperature environments. This deficiency in stability can be notably improved by hydrogenating the conjugated diene polymers in order to eliminate the residual double bonds that persist within the polymer chains.

With the availability of a large number of unsaturated polymers of differing microstructures, the selective reduction of carbon-carbon double bonds offers a means of producing a wide variety of specialty polymers. By reducing the unsaturation level of the polymers, their physical properties – such as tensile strength, elongation, thermal stability, light stability and solvent resistance – may be optimized. For example, the removal of the C=C unsaturation 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 (Scheme 19.2a). 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 (Scheme 19.2b). This modified polymer has greatly increased thermal and oxidative stability, together with processability and serviceability at higher temperature, by virtue of its poly(ethylene-*co*-butylene) center block. The catalytic hydrogenation of acrylonitrile-butadiene rubber (NBR) (Scheme 19.2c) is an especially important commercial example, resulting in its tougher and more stable derivative, hydrogenated nitrile butadiene rubber (HNBR), which has been widely used in the automotive industry.

Numerous methods have been employed for hydrogenating conjugated diene-based polymers in the presence of suitable and effective hydrogenation catalysts. Typical hydrogenation catalysts can be classified into two types: heterogeneous and homogeneous catalysts.



Scheme 19.2 (a) Hydrogenation of polybutadiene.
 (b) Hydrogenation of the copolymer of butadiene and styrene.
 (c) Hydrogenation of acrylonitrile butadiene rubber.

19.1.2.1 Heterogeneous Catalysts

Heterogeneous catalysts, which are not soluble in the diene-based polymers to be hydrogenated, have involved metals such as nickel, platinum, or palladium deposited onto supports such as activated carbon, silica, alumina, or calcium carbonate. Hydrogenation using a heterogeneous catalyst is described as follows. 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, 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 chain. In addition the polymer, once hydrogenated, tends to remain on the

surface of the catalyst and to interfere with subsequent access to active centers of the catalyst with the non-hydrogenated polymer.

The hydrogenation also requires higher temperature and pressure, and hence decomposition of the polymer and gelation of the reaction system often tends to occur. For the hydrogenation of a copolymer of a conjugated diene with a vinyl aromatic hydrocarbon, even hydrogenation of the aromatic ring portion may take place to some extent due to the high temperature and hydrogen pressure. Thus, it is often difficult to selectively hydrogenate only the double bonds in the conjugated diene portion of the polymer. Although widely used in industry, heterogeneous catalysts generally have lower activity than homogeneous catalysts, and usually a larger amount of heterogeneous catalyst is required. Furthermore, since the polymer may be strongly adsorbed onto the heterogeneous catalyst, it is impossible to completely remove the catalyst from the hydrogenated polymer solution, although the separation of catalyst from heterogeneous catalytic systems is usually easier than from homogeneous ones.

19.1.2.2 Homogeneous Catalysts

Homogeneous catalysts, which are soluble in the solutions of the diene-based polymers to be hydrogenated, include:

- Ziegler-type catalysts obtained from an organic acid salt or acetylacetonate salt of nickel, cobalt, iron, or chromium which reacts with a reducing agent such as an organic aluminum compound.
- Metallocene complexes.
- Organometallic catalysts containing Ru-, Rh-, Os-, Ir-, Pd-complexes, etc.

The reaction operation using a homogeneous catalyst is similar to that using heterogeneous catalysts, except for the nature of the contact between the catalyst and the polymer. First, the polymer to be hydrogenated is dissolved in a suitable solvent. The catalyst can be prepared in a solution or solid form. Then, the catalyst is mixed with the polymer solution in the presence of hydrogen. During hydrogenation of the polymer, contact between the polymer and catalyst is much more effective compared to a heterogeneous catalyst system. Therefore, compared to the heterogeneous catalyst, the homogeneous catalyst generally shows higher activity, and only a small amount of catalyst enables hydrogenation to be effected at mild temperature and low pressure. In addition, homogeneous catalysts usually have high selectivity. When appropriate hydrogenation conditions are selected, it is possible to preferentially hydrogenate the conjugated diene portion of a copolymer of a conjugated diene with a vinyl aromatic hydrocarbon, while not hydrogenating the aromatic ring portion. Compared to heterogeneous catalysis, the disadvantage of homogeneous catalysis is that the catalyst recovery from a homogeneous system is often much more difficult than from a heterogeneous system. Therefore, in recent years, a new class of catalysts termed "heterogenized homogeneous catalysts" have received significant attention and have become an area of extensive research interest.

This chapter provides a review of the progress in reaction art, reactor techniques and process technology with respect to homogeneous catalytic hydrogenation of diene-based polymers, in accordance with the homogeneous hydrogenation theme of this handbook.

19.2

Reaction Art

19.2.1

Catalyst Techniques

Although the overall polymer hydrogenation reaction is exothermic, a high activation energy prevents it from taking place under normal conditions in the absence of a catalyst. An efficient catalyst is needed to circumvent this restriction and it is in fact the key in realizing a successful homogeneous hydrogenation. Metals from Group VIII B (e.g., platinum, palladium, nickel, rhodium, ruthenium, iridium, osmium) and from Group IV (e.g., titanium) are among the most widely used hydrogenation catalysts, and they usually can be activated for hydrogenation at a temperature of less than 200 °C.

An early US Patent [1] disclosed that the catalyst $\text{RhHCO}(\text{PPh}_3)_3$ was effective for a limited degree of hydrogenation of PB. However, because of the very low reaction temperature and hydrogen pressure employed (25 °C, 2 atm, 3 h), the concentration of catalyst used was about 1100 μM , which was very high compared to the level now used in industrial polymer hydrogenation processes. Moreover, the hydrogenation degree was very low where mainly some of the vinyl C=Cs were hydrogenated. However, it indicated there was some degree of efficacy of the rhodium catalyst in hydrogenating PB. The low hydrogenation efficiency was successfully overcome for the hydrogenation of diene-based polymers by increasing the hydrogenation temperature to 110 °C or higher [2], in which a much lower catalyst concentration was used and a hydrogenation degree of 99.95% was achieved.

Research in this area over the past 30 years has focused on the design of efficient catalytic systems and on improving the hydrogenation operations. Besides rhodium-based species, a variety of catalysts has been investigated for the homogeneous hydrogenation of diene-based polymers, including Os-, Ru-, Ir-, Ni- and Ti-based catalysts. The patents most relevant to the hydrogenation technology of diene-based polymers are summarized in Table 19.1.

Two critical reviews with respect to polymer hydrogenation have been published [63, 64]. Among the investigated catalysts, Wilkinson's catalyst ($\text{RhCl}(\text{PPh}_3)_3$) is still considered as the most preferable for the hydrogenation of diene-based polymers as it provides high selectivity towards the olefin double bonds with minimized crosslinking problems. The only concern for using the rhodium catalyst is its relatively high cost.

In order to overcome the catalyst recovery problem in homogeneous hydrogenation operations, the significant enhancement of catalyst activity has been pur-

Table 19.1 Outline of major patents with respect to catalysts for diene-based polymer hydrogenation.

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
RhHCO(PPh ₃) ₃ ; RuHCl(PPh ₃) ₃	PB	PB in toluene (2.3 wt.%); RhHCO(PPh ₃) ₃ : 5 g per 100 g PB; P _{H2} : 0.2 MPa; T: 25°C; t: 3 h; Conversion: 10.4%	The Firestone Tire & Rubber Company (Akron, USA)	1 (1976)
RhH(PPh ₃) ₄ ; RhCl(PPh ₃) ₃ /epoxidized soybean oil (R ¹ OCH ₂ CH(OR ²)CH ₂ R ³)	NBR, SBS, methacrylic acid-acrylonitrile – butadiene copolymer	NBR in chlorobenzene (2.5 wt.%); RhH(PPh ₃) ₄ : 1 g per 100 g NBR; PPh ₃ : 10 g per 100 g NBR; P _{H2} : 2.8 MPa; T: 160°C; t: 1 h; Conversion: >99%	Polysar Limited/Bayer Inc. (Sarnia, Canada)	2 (1984) 3 (1985) 4 (2004)
OsHX(CO)(L)(PR ₃) ₂ , where X: Cl, BH ₄ or CH ₃ COO; L: O ₂ or no ligand; R: cyclohexyl or isopropyl	NBR, styrene butadiene random copolymer (SBR), methacrylic acid- acrylonitrile – butadiene copolymer	NBR in chlorobenzene (2.4 wt.%); OsHCl(CO)(P(cyclohexyl) ₃) ₂ : 0.25 g per 100 g NBR; P _{H2} : 2.07 MPa; T: 130°C; t: 1 h; Conversion: 99.3%	University of Waterloo (Waterloo, Canada)	5 (1996)
RuX _m (L ¹)(L ²) _n , where X: H, Halogen or SnCl ₃ , etc.; L ¹ : H, Halogen or substituted indenyl, etc.; L ² : phosphane or arsane, etc.	NBR	NBR in butanone (9.7 wt.%); RuCl ₂ (PPh ₃) ₃ : 0.16 g per 100 g NBR; P _{H2} : 14 MPa; T: 130°C; t: 4 h; Conversion: 99.7%	Bayer Aktiengesellschaft (Leverkusen, Germany)	6 (1986) 7 (1989) 8 (1991)

Table 19.1 (continued)

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
HRuCl(CO)(PPh ₃) ₃ ; RuCl ₂ (PPh ₃) ₃ ; RuH ₂ (CO)(PPh ₃) ₃ , etc.	NBR, SBS, styrene butadiene diblock copolymer (SB), acrylonitrile- isoprene copolymer	NBR in chlorobenzene (1.7 wt.%); HRuCl(CO)(PPh ₃) ₃ : 0.8 g per 100 g NBR; C ₂ H ₅ COOH: 0.2 g per 100 g NBR; P _{H₂} : 4.1 MPa; T: 140 °C; t: 1.8 h; Conversion: >99%	University of Waterloo (Waterloo, Canada)	9 (1989) 10 (1989) 11 (1991)
HRuCl(CO)(PCy ₃) ₃ , etc./ Amine(RNH ₂)	NBR	NBR in chlorobenzene (1.7 wt.%); HRuCl(CO)(PCy ₃) ₃ : 0.05 g per 100 g NBR; octylamine: 0.39 g per 100 g NBR; P _{H₂} : 5.5 MPa; T: 145 °C; t: 5 h; Conversion: >99%	University of Waterloo (Waterloo, Canada)	12 (1991)
HRuCl(CO)(PPh ₃) ₃ , etc.	Ring-opening polymers	Poly(8-methyl-8-methoxy-carbonyltetracyclo- 3-dodecene) in toluene (20 wt.%); HRuCl(CO)(PPh ₃) ₃ : 0.01 g per 100 g polymer; P _{H₂} : 4.0 MPa; T: 160 °C; t: 4 h; Conversion: 99.7%	Japan Synthetic Rubber Co., Ltd. (Tokyo, Japan)	13 (1993)
RuCl ₂ (PPh ₃) ₄ , etc.	Ring-opening me- tathesis polymers	Polymer in tetrahydrofuran (11.4 g L ⁻¹); RuCl ₂ (PPh ₃) ₄ : 0.05 g per 100 g polymer; Et ₃ N: 0.021 g per 100 g polymer; P _{H₂} : 8.3 MPa; T: 165 °C; t: 5 h; Conversion: 100%	Mitsui Chemicals Inc. (Tokyo, Japan)	14 (1999)

Table 19.1 (continued)

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
Bimetallic complexes, Rh/Ru (RhCl(PPh ₃) ₃ /RuCl ₂ (PPh ₃) ₃), etc.	NBR	NBR in xylene (7 g per 100 mL); RhCl(PPh ₃) ₃ /RuCl ₂ (PPh ₃) ₃ (Rh:Ru = 3:1, mole ratio): 0.4 g per 100 g NBR, PPh ₃ : 2 g per g catalyst; P _{H₂} : 0.8 MPa; T: 145 °C; t: 4 h;	Nantex Industry Co., Ltd., (Taiwan)	15 (2000)
Nickel acetylacetonate ((CH ₃ COCH=C(O)CH ₃) ₂ Ni)/ <i>p</i> -nonylphenol (C ₉ H ₁₉ C ₆ H ₄ OH)/ <i>n</i> -butyllithium (CH ₃ (CH ₂) ₃ Li)	Polysisoprene, EPDM	Conversion: 98.5% Polysisoprene in hexane (2.5 wt.%); Catalyst (Nickel acetylacetonate: <i>p</i> -nonylphenol: <i>n</i> -butyllithium = 8:8:25, mol ratio): 4 mmol nickel per 100 mL solution; P _{H₂} : 0.34 MPa; T: room temperature; t: 0.8 h;	Uniroyal Inc. (New York, USA)	16 (1976)
Cobalt or nickelbenzohydroxamic acid (C ₆ H ₅ CONH-O) ₂ M, M = Co, Ni/ organoaluminum (R ₃ Al, R = alkyl)	PB, SBR	Conversion: 78% SBR in hexane (10 wt.%); Catalyst (nickel benzohydroxamic acid: triisobutyl aluminum = 1:3, mol ratio): 0.01 mmol Ni per g SBR; P _{H₂} : 1.4 MPa; T: 180 °C; t: 2 h; Conversion: 99%	The Firestone Tire & Rubber Company (Akron, USA)	17 (1976)

Table 19.1 (continued)

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
Nickel-2-ethylhexanoate ((CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)(CO ₂) ₂ Ni)/ alkylaluminum (R ₃ Al, R = alkyl) or alkylalumoxane ((-Al(R)O) _n) or hydrocarbyl-substituted silicon alumoxane (Et ₂ AlO) ₂ SiO ₂ , etc.)	SBS, Styrene-butadiene-isoprene copolymers	SBS in cyclohexane (18 wt.%); Catalyst (nickel-2-ethylhexanoate/triethyl aluminum, Al:Ni = 2.2:1, atomic ratio): 0.05 g Ni per 90 g SBS; P _{H₂} : 6.2 MPa; T: 90 °C; t: 3 h; Conversion: 93.4%	Shell Oil Company (Houston, USA)	18 (1991) 19 (1991) 20 (1991) 21 (1989) 22 (1991)
Nickel acetylacetonate ((CH ₃ COCH=C(O-)CH ₃) ₂ Ni)/alkylaluminum (R ₃ Al, R = alkyl)	SBR	SBR (0.9 L BD + 0.5 L ST anionic polymerization) in 4.8 L cyclohexane; Catalyst: 0.3 g nickel acetylacetonate (in 9 mL toluene) + 11 mL aluminum triisobutyl solution (10% in hexane); H ₂ O: 14 mol per mol Ni; P _{H₂} : 1 MPa; T: 25–30 °C; t: 1 h; Conversion: 93.4%	BASF Aktiengesellschaft (Germany)	23 (1980)
Nickel bis(acetylacetonate) or 2-ethylhexanoic acid nickel ((CH ₃ COCH=C(O-)CH ₃) ₂ Ni or (CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)(CO ₂) ₂ Ni)/alkylaluminum (R ₃ Al, R = alkyl)	Styrene-isoprene-styrene block copolymer (SIS), polyisoprene, PB	PB in cyclohexane (20 wt.%); Catalyst (2-ethylhexanoic acid nickel/triisobutyl aluminum, Ni:Al = 1:3): 0.74 mol Ni per 100 g PB; P _{H₂} : 0.98 MPa; T: 70–80 °C; t: 6 h; Conversion: 97%	Kuraray Co., Ltd. (Tokyo, Japan)	24 (2002) 25 (2002) 26 (2003)

Table 19.1 (continued)

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
Nickel or Cobalt acetylacetonate ((CH ₃ COCH=C(O)CH ₃) _n) ₂ M, n=2,3; M= Ni, Co)/alkylaluminum (R ₃ Al, R=alkyl); titanium compounds (Cp ₂ TiCl ₂ , etc.)/organoaluminum (R ₃ Al, etc., R=alkyl) or organolithium (RLi, R=alkyl)	Metathesis polymers	Poly(dicyclopentadiene) in cyclohexane (7.6 wt.%); Catalyst (cobalt(III) acetylacetonate: triisobutyl- aluminum = 1.9: 4.2, weight ratio): 0.2 g per g polymer; P _{H2} : 0.98 MPa; T: 60 °C; t: 0.5 h; Conversion: 99.9%	Nippon Zeon Co., Ltd (Tokyo, Japan)	27 (1996)
Cobalt-2-ethylhexanoate ((CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)CO ₂) ₂ Co)/ alkylaluminum (R ₃ Al, R=alkyl)	Polymers containing ketone groups	SBS (include ketone groups) in cyclohexane (~ 5 wt.%); Catalyst (cobalt-2-ethylhexanoate: triethyl aluminum = 1: 3.9, weight ratio): [Co] = 880 ppm (added in increments); P _{H2} : 3.45 MPa; T: 70–90 °C; t: 6 h; Conversion: 78%	Shell Oil Company (Houston, USA)	28 (1996) 29 (1997)
Palladium-2-ethylhexanoate ((CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)CO ₂) ₂ Pd)/ organoaluminum ((-Al)(CH ₃ O) _n)	NBR	NBR in methylethyl ketone (5 wt.%); Catalyst (palladium-2-ethylhexanoate/methyl alumoxane, Al: Pd = 0.7: 1, atomic ratio): 8.5 mmol Pd per lb NBR; P _{H2} : 6.2 MPa; T: 60 °C; t: 2 h; Conversion: 90%	Shell Oil Company (Houston, USA)	30 (1989) 31 (1989)

Table 19.1 (continued)

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
Titanocene ($\text{Cp}_2\text{Ti}(\text{R}^1)\text{R}^2$) (R^2)(R^3) $\text{C}_6\text{H}_2(\text{R}^4)(\text{R}^5)(\text{R}^6)$, $\text{R}^1 \sim \text{R}^6$: alkyls or hydrogen atoms)	PB, polyisoprene, styrene/isoprene or butadiene co- polymers	SBS in cyclohexane (5 wt.%); Catalyst (di- <i>p</i> -tolyl- bis(<i>η</i> -cyclopentadienyl) titanium): 4 μM ; P_{H_2} : 0.49 MPa; T : 90 °C; t : 2 h; Conversion: 99%	Asahi Kase Kogyo Kabushiki Kaisha (Osaka, Japan)	32 (1987)
Titanocene ($\text{Cp}_2\text{Ti}(\text{R}^1)\text{R}^2$, R^1 and R^2 : halogen atoms, aryloxy groups, etc.)/ alkyloxy lithium (R^3OLi , R^3 : a hydro- carbon group, etc.); Titanocene or zir- conocene $\text{Cp}_2\text{M}^1(\text{R}^1)\text{R}^2$, M^1 : Ti or Zr; R^1 and R^2 : halogen atoms, aryloxy groups, etc.)/organoalkali (M^2OR^4 , M^2 : alkali metal, R^4 : alkyl group, etc.)/ organoaluminum or organomagne- sium ($\text{M}^2\text{M}^3\text{R}^5$, M^2 : alkali metal; M^3 : Al or Mg; n : 3, 4; R^5 : halogen, alkyl, aryl or alkoxy group, etc.)	SB, SBS, SIS	SB in cyclohexane (20 wt.%); Catalyst (bis(cyclopentadienyl) titanium dichlo- ride: 2,6-di- <i>n</i> -butyl-4-methylphenoxy/lithium = 1 : 6, mole ratio): 25 $\mu\text{mol Ti}$ per 100 g SB; P_{H_2} : 0.98 MPa; T : 70 °C; t : 1 h; Conversion: 99%	Japan Synthetic Rubber Co. Ltd. (Tokyo, Japan)	33 (1990) 34 (1992)
Titanocene ($\text{Cp}_2\text{Ti}(\text{R}^1)\text{R}^2$, etc., R^1 and R^2 : halogen atoms, aryloxy groups, etc.) or Tebbe's reagent $\left(\text{Cp}_2\text{Ti} \begin{array}{c} \text{Cl} \\ \diagdown \quad \diagup \\ \text{CH}_3 \quad \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \end{array} \right) / \text{co-catalyst}$ and/or promoter (LiR, R: alkyl, etc.)	Styrene, buta- diene and/or iso- prene living copolymers	SBS in cyclohexane (18 wt.%); Catalyst (2,5-diphenylphospholyl (cyclopentadie- nyl) titanium dichloride): 0.5 mg per g SBS; P_{H_2} : 1 MPa; T : 70 °C; t : 3 h; Conversion: 100%	Shell Oil Company (Houston, USA)	35 (1992) 36 (1992) 37 (1992) 38 (1992) 39 (1993) 40 (1994) 41 (1998) 42 (1999) 43 (1999) 44 (2002)

Table 19.1 (continued)

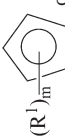

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
Titanocene or Zirconocene ($(A)(E)M(R^1)^2$; A and E represent:	Polyisoprene	Polyisoprene in bromobenzene (8 wt.%); Catalyst ($Cp^*Cp(tBu)ZrMe_2$; (Ph_3C)($B(C_6F_5)_4$) $=1.1:1$, mole ratio): 60 μ mol per g polymer; P_{H_2} : 0.1 MPa; T: not available; t: 0.75 h; Conversion: 100%	Shell Oil Company (Houston, USA)	45 (1999)
 or 				
R ¹ –R ⁴ : halogens, hydrocarbonyl groups, etc./non-coordinating stable anion (B(AT) ₄ ; Ar: C ₆ F ₅ , etc.) Rare earth (Sm) metallocene (Cp_2SmR)/organolithium (LiR, etc.)	SBS	SBS in cyclohexane (5 wt.%); Catalyst (<i>sec</i> -butyllithium: (Cp^*Cp^*SmH) ₂ $=7.5:1$, mole ratio): 2.6 mmol per 100 g SBS; P_{H_2} : 3.45 MPa; T: 40–66 °C; t: 3 h; Conversion: 81%	Shell Oil Company (Houston, USA)	46 (1992)
Rare earth (Sm) metallocene ($(C_5R_5)_2SmX$, X is an inert substituent capable of replacement by hydrogen)	PB	PB in cyclohexane (1.4 wt.%); Catalyst (bis(pentamethylcyclopentadienyl) (bis(trimethylsilyl)methyl) samarium: 0.018 g per g PB; P_{H_2} : 2.8 MPa; T: 90 °C; t: 3 h; Conversion: 99.5%	The Dow Chemical Company (Midland, USA)	47 (1992)

Table 19.1 (continued)

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
Monocyclopentadienyl titanium compound (R_nCpSmL_m , R: anion or dianion non-Cp group; L: neutral ligand)	SBR, PB	PB in cyclohexane (~10 wt.%); Catalyst (pentamethylcyclopenta-dienyl tribenzyl titanium): 0.66 mmol per 100 g PB; P_{H_2} : 2.1 MPa; T : 55 °C; t : 24.6 h; Conversion: 71%	The Dow Chemical Company (Midland, USA)	48 (1998)
Metalocene ($CpCp^*MD$, M: metal; D: conjugated, neutral diene)	Unsaturated polymers		The Dow Chemical Company (Midland, USA)	49 (2002)
Monocyclopentadienyl titanium compound ($CpTi(R^1)(R^2)R^3$, $R^1 \sim R^3$: non-Cp groups)	SBS, SBR, PB, SIS	SBS in cyclohexane (12.5 wt.%); Catalyst ($CpTiCl_2(OC_5NH_4)$): 0.4 mmol per 100 g SBS; P_{H_2} : 0.98 MPa; T : 80 °C; t : 3 h; Conversion: 99.4%	Korea Kumho Petrochemical Co., Ltd. (Seoul, Rep. of Korea)	50 (1999) 51 (1999) 52 (2000) 53 (2002)
Titanocene ($Cp_2Ti(PhOR)_2$ or Cp_2TiR_2)	PB, SBS, SB	SBS in cyclohexane (2 wt.%); Catalyst ($Cp_2Ti(4-CH_3OPh)_2$): 4 mmol per 100 g SBS; P_{H_2} : 0.59 MPa; T : 85 °C; t : 2 h; Conversion: 91%	Repsol Quimica S.A. (Madrid, Spain)	54 (1996)
Zirconocene (Cp_2ZrR_2 , R: halogen or alkyl group, etc.)/ alumoxane ($(-Al(CH_3)O)_n$, etc.)	SBS (star-form)	SBS in toluene (5.5 wt.%); Catalyst (Cp_2ZrCl_2 /methylalumoxane, Zr:Al = 1:118, atomic ratio): 3.08 mmol Zr per 100 g SBS; P_{H_2} : 2 MPa; T : 90 °C; t : 0.65 h; Conversion: 80%	Neste Oy (Provoo, Finland)	55 (1998)

Table 19.1 (continued)

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
Cobaltocene or Nickelocene (Cp_2MR_2 , M: metal)/Organic lithium (LiR, etc.)	SBS	SBS in cyclohexane (5.8 wt.%); Catalyst (bis(cyclopentadienyl) cobalt(II)/butyllithium): 4.1 mmol Co per 100 g SBS; P_{H_2} : 2.45 MPa; T : 80 °C; t : 2 h;	Taiwan Synthetic Rubber Corporation (Taiwan)	56 (1998)
Titanocene (Cp_2TiR_2)/silyl hydride ($RSiO-(SiH(R)O)_nSiR_3$, etc.)	SBS	Conversion: 99.2% SBS in cyclohexane (13 wt.%); Catalyst (Cp_2TiMe_2 : ethylhydrocyclosiloxane = 1:1.5, mole ratio): 0.08 mmol per 100 g SBS; P_{H_2} : 1.4 MPa; T : 60 °C; t : 1 h;	Industrial Technology Research Institute (Taiwan), Chi Mei Co. (Taiwan)	57 (2001)
Titanocene (Cp_2TiR_2)/organoderivate (MR_2 , M: Mg or Zn)/modifier (ROR, etc.) or another organoderivate (AlR_3)	Styrene, buta- diene and/or iso- prene copolymers	Conversion: 99% SBS in cyclohexane (12.5 wt.%); Catalyst (bis-cyclopentadienyltitanium dichloride: 1,2-di- <i>n</i> -butoxy-ethane: diisobutyl magnesium = 1:0.1:0.25, mole ratio): 0.19 mmol per 100 g SBS; P_{H_2} : 0.49 MPa; T : 70 °C; t : 1 h;	Enichem S.p.A. (Milan, Italy)	58 (1999) 59 (2001)
Titanocene (Cp_2TiR_2)	SBS, SIS	Conversion: >98% SBS in cyclohexane (12.5 wt.%); Catalyst ($Cp_2Ti((C_5H_8)_2C_4H_9)$): 0.2 mmol Ti per 100 g SBS; P_{H_2} : 0.8 MPa; T : 100 °C; t : 0.5 h; Conversion: >98%	Enichem S.p.A. (Rome, Italy); Polimeri Europa S.p.A. (Brindisi, Italy)	60 (2004)

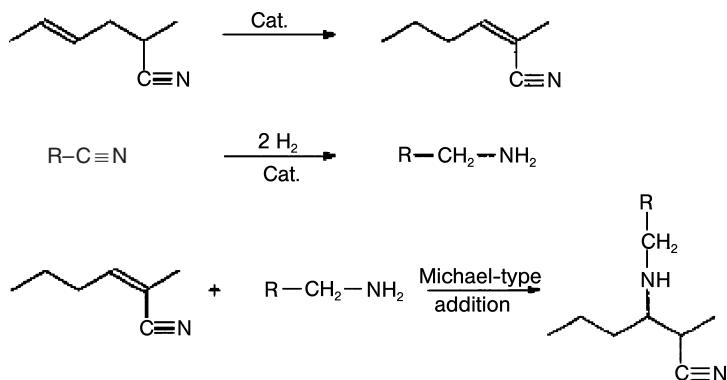
Table 19.1 (continued)

Catalyst	Polymer	Representative example ^{a)}	Assignee	Reference (Year)
Titanocene (Cp_2TiR_2)/titanium alkoxide (R_3TiOR)/trialkylaluminum (AlR_3)	SBS	SBS in cyclohexane (9.7 wt.%); Catalyst [titanium(IV) isopropoxide: bis(cyclopentadienyl) titanium dichloride: triisobutyl aluminum = 1:0.5:3, mole ratio]: 0.17 mmol Ti per 100 g SBS; P_{H_2} : 2.5 MPa; T : 80 °C; t : 1 h; Conversion: 97%	TSRC Corporation (Taiwan)	61 (2005)
Titanocene (Cp_2TiR_2)/alkylaluminum (LiR)	Styrene, butadiene or isoprene copolymers	PB in cyclohexane and toluene (5 wt.%); Catalyst [bis(cyclopentadienyl) titanium dichloride]: 0.4 mmol per 100 g PB; P_{H_2} : 0.49 MPa; T : 40 °C; t : 2 h; Conversion: 97%	Asahi Kasei Kogyo Kabushiki Kaisha (Osaka, Japan)	62 (1985)

P_{H_2} : pressure of hydrogen; T : temperature; t : time.

sued such that the amount of catalyst required may be significantly reduced. Parent et al. [65] described the selective hydrogenation of C=C within NBR using the homogeneous catalyst precursor, $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in solution, which has a high hydrogenation activity for hydrogenation of NBR as well as poly-isoprene [66]. 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. Pan and Rempel [67] described an efficient catalytic system for the hydrogenation of styrene-butadiene rubber (SBR) in solution using a ruthenium complex $(\text{Ru}(\text{CH}=\text{CHPh})\text{Cl}(\text{CO})(\text{PCy}_3)_2)$, where Ph=phenyl, Cy=cyclohexyl). Because of the high efficiency of the ruthenium catalyst, the catalyst required to realize the hydrogenation is used at a very low level. Indeed, even if all of the catalyst were to be retained in the final products the metal residue would still be less than 7 ppm. Ruthenium-based catalysts have also been used for the hydrogenation of NBR [6–12, 15, 68], polyisoprene [68, 69] and PB [68, 70]. As with the osmium-based catalyst, the ruthenium-based catalysts are efficient but more susceptible with respect to causing crosslinking in NBR during hydrogenation. The mechanism of crosslinking is not well understood. Although a Michael-type addition mechanism (see Scheme 19.3) was speculated to account for this problem, and there were some signs to support this mechanism (e.g., the hydrogenation of NBR catalyzed by ruthenium-based catalysts in the presence of an amine helped to suppress crosslinking [12]), this mechanism has not been substantiated by definitive experimental results [71].

Hsu et al. [15] applied a bimetallic catalyst comprising rhodium and ruthenium for the hydrogenation to combine the high selectivity of the rhodium complex with the lower cost of the ruthenium complex. When the amount of each metal is identical, the catalytic activity of the bimetallic complex catalyst system was similar to that of the single rhodium-complex catalyst, containing



Scheme 19.3 Michael-type addition mechanism for nitrile butadiene rubber (NBR) crosslinking [71].

the same total amount of metal. However, since part of the rhodium is substituted by ruthenium, the bimetallic catalyst becomes less expensive.

Few reports have been published on the hydrogenation of diene polymers using iridium complexes. Gilliom [72] and Gilliom and Honnell [73] described the use of $[\text{Ir}(\text{COD})\text{L}_2]\text{PF}_6$, where COD=cyclooctadiene and L=a phosphine, for the hydrogenation of bulk PB. It was found that $[\text{Ir}(\text{COD})(\text{PMePh}_2)_2]\text{PF}_6$, where Me=methyl and Ph=phenyl, when compared with Wilkinson's catalyst, resulted in a faster hydrogenation than the rhodium complex in the early stages of the reaction; however, the degree of hydrogenation achieved was less than that with the Wilkinson's catalyst. This study presented a rare example of polymer hydrogenation occurring in a pure polymer matrix. In this case an organic solvent was used initially to disperse the catalyst into the polymer matrix, with subsequent removal of the solvent before the hydrogenation operation.

Some examples of the hydrogenation of unsaturated rubber catalyzed by palladium complexes have been reported by Bhattacharjee et al. [74–78]. When palladium acetate ($(\text{CH}_3\text{CO}_2)_2\text{Pd}$) was used as a catalyst for the hydrogenation of NBR [74] and styrene-isoprene-styrene triblock copolymer (SIS) [75], the catalyst showed good selectivity. However the observed maximum conversion was 96% for NBR and 90% for SIS. This catalyst also showed activity for the hydrogenation of natural rubber and epoxidized natural rubber [76]. The results showed that the catalyst was highly selective in reducing olefinic unsaturation in the presence of epoxy groups, and an increase in the epoxy content of the rubber resulted in a decrease in hydrogenation rate and a decrease in the maximum attainable hydrogenation level. Another palladium complex, namely, a six-membered cyclopalladate complex of 2-benzoyl pyridine ($(\text{Pd}(\text{CH}_3\text{COO})(\text{C}_6\text{H}_5\text{COC}_5\text{H}_4\text{N}))_2$), was used as catalyst for the selective hydrogenation of NBR, carboxylated nitrile rubber (XNBR) and PB [77, 78]. The reported maximum conversion of C=C using this complex was lower than that obtained with palladium acetate. The main drawback of the palladium complex catalysts is that the degree of hydrogenation achieved cannot satisfy the commercial requirement.

One type of Ziegler-catalyst system, used for polymer hydrogenation, consisted of an organic acid salt or acetylacetonate salt of Ni, Co, Pd, etc. and a reducing agent such as an organoaluminum compound. Nickel-based catalysts, such as nickel 2-ethyl hexanoate ($(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2)_2\text{Ni}$)/triisobutyl aluminum ($(\text{CH}_3)_3\text{CH}_2\text{Al}$), nickel acetylacetonate ($(\text{CH}_3\text{COCH}=\text{C}(\text{O})\text{CH}_3)_2\text{Ni}$)/triisobutyl aluminum, and nickel benzohydroxamic acid ($(\text{C}_6\text{H}_5\text{CONH-O})_2\text{M}$, M=Co, Ni)/triisobutyl aluminum, demonstrated activities for the hydrogenation of PB, SBR, and polyisoprene [16, 17, 79]. The Shell Oil Company (Houston, Texas) has filed a series of patents for the application of a Ni/Al catalyst system [18–22]. Besides nickel, cobalt [27–29] and palladium [30, 31] salts together with alkylaluminum compounds or alkylalumoxane have also been used as catalyst systems for polymer hydrogenation. The chief benefit of these systems is that they are relatively inexpensive in terms of the cost of metals used. However, these types of catalysts and co-catalysts need to be used at relatively high concentration in order to achieve favorable reaction rates at the chosen reaction

conditions due to their relative lower activities compared with organometallic catalysts containing Pt-group metals. The high metal concentration in the solution is also a major obstacle when removal of the metal is necessary, as the residual catalyst adversely affects the stability of the hydrogenated product and is detrimental to various applications. Another drawback of these types of catalysts is their poor selectivity as hydrogenation of both ethylenic and aromatic unsaturation may occur, though under certain conditions they show some degree of selectivity for the hydrogenation of ethylenic unsaturations as a result of steric hindrance [21, 22].

Another type of Ziegler-catalyst, which was investigated for polymer hydrogenation, is that of metallocene catalysts. These catalysts consist mainly of halides or aryls of cyclopentadienyl Group III or IV metals (e.g., $\text{RMX}^1\text{X}^2\text{X}^3$, where R is an unsubstituted or substituted cyclopentadienyl group; M is metal; X^1 , X^2 and X^3 may be either the same or different selected from halogen atoms, aryl groups, aryloxy groups or carbonyl groups, etc., and one of them may be an unsubstituted or substituted cyclopentadienyl group) which are often treated with organolithium reducing agents, and have been applied for homogeneous polymer hydrogenation [32–62, 80]. The most widely used of these catalysts are substituted or unsubstituted bis(cyclopentadienyl)-titanium compounds; however, zirconium and hafnium complexes have also been reported for the purpose of polymer hydrogenation [34, 45, 55]. When these titanocene-based catalysts are used for the hydrogenation of unsaturated living polymers, the hydrocarbon lithium or lithium hydride compounds which are produced from the termination reactions of the hydrocarbon or hydrogen with the alkyl lithium initiator serve as a reducing agent for the hydrogenation catalyst. In this case, the addition of an organolithium compound which is necessary for reduction of the complex during the hydrogenation process can be omitted [35–38, 41–44]. In this catalyst system, when the alkyl-lithium complex (lithium hydride generated *in situ*) or the alkoxy lithium compound is used to activate the bis(cyclopentadienyl) titanium catalyst for effective hydrogenation of polymers, an excess amount of the lithium species may also induce reduction of the titanium compounds, resulting in decomposition of the catalyst component as well as a reduction in catalyst activity. In this case some reagents such as ethanol or difluorodiphenyl silane can be added to the system to adjust the ratio of lithium hydride to titanium [37, 44]. Some of these catalysts may be used without the addition of Group I, II, IIIA alkyl compounds such as substituted titanocene biaryl compounds, etc. [32, 54].

Related to these catalysts are the systems based on lanthanide metal systems or rare earth metal complexes [46, 47]. The main problem with these catalyst systems is their instability. When the catalyst solution is prepared by reacting a metallocene with an organolithium compound in a polar solvent, the prepared catalyst solution is unstable and decomposes quickly, even under a nitrogen atmosphere. The activity of these catalysts can be high only if the catalyst is added to the polymer solution immediately after preparation. Attempts have been made to overcome the stability problem by using an additive in the system to improve the stability and the activity of the catalyst [33–35, 41, 57, 58, 61]. Re-

cently, it was also found that monocyclopentadienyl titanium compounds are more stable and less sensitive to the extra lithium hydride [50–53] than bis(cyclopentadienyl) titanium compounds. Another disadvantage of the above catalysts is that the Group III and IV metal halides (as well as the lithium halides) formed from the catalyst system tend to corrode the metal reactors used in the hydrogenation process. This results in increased investment costs to provide expensive, corrosion-resistant metal alloy reactor systems. It may be possible to overcome such a problem by replacing the titanium with a Group VIIIB metal such as cobalt or nickel [56], as no corrosion of the reactor system was observed when a bis(cyclopentadienyl) cobalt (or nickel) complex and an organolithium compound were used as a catalyst system for the hydrogenation of polymers. Furthermore, this cobalt or nickel catalyst system showed much higher stability than the titanocene catalysts. In fact, the bis(cyclopentadienyl) cobalt(II)/*n*-butyllithium catalyst still had high activity for the hydrogenation of the polymer two weeks after it was prepared and stored under nitrogen.

The metallocene catalysts have good selectivity and high activity under mild reaction conditions. Given these advantages, it is to be expected that these systems would show promise for the homogeneous hydrogenation of polymers on a commercial scale. However, there is no report on the application of this catalyst for the hydrogenation of NBR. One possible reason for this is that the polar (CN) groups in NBR may bond to the active metal center and deactivate the catalyst.

19.2.2

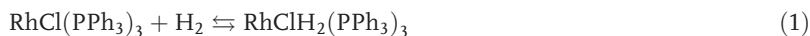
Hydrogenation Kinetic Mechanism

An understanding of the kinetics and catalytic mechanism of polymer hydrogenation is essential in order to optimize the reaction conditions, to control the reaction systems, and to design commercial production processes. Catalytic kinetic mechanisms for Rh-, Os- and Ru-complex polymer hydrogenation systems have been extensively investigated, and are summarized in the following sections.

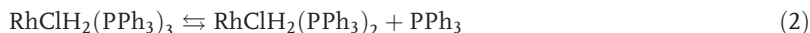
19.2.2.1 Rhodium-Based Catalysts

$\text{RhCl}(\text{PPh}_3)_3$ has been used for the homogeneous hydrogenation of various diene-based polymers, and its catalytic mechanism is understood to a considerable extent. Parent et al. [81] proposed a mechanism which has been found to be consistent with the kinetic data for various diene-based polymer hydrogenation systems and an understanding of the coordination chemistry of $\text{RhCl}(\text{PPh}_3)_3$ in solution. The main points comprising the mechanism are outlined as follows:

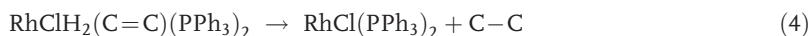
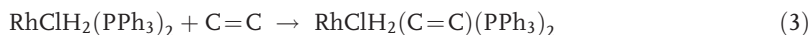
- $\text{RhCl}(\text{PPh}_3)_3$ oxidatively adds molecular hydrogen to form a five-coordinate dihydride complex which is consistent with the previous understanding [82] for olefin hydrogenation. This was also confirmed by experiments conducted by Mohammadi and Rempel [83] for NBR hydrogenation, where at 65 °C under 1 bar H_2 the reaction is quantitative towards formation of the dihydride:



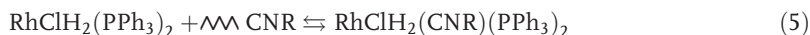
- The dissociation of phosphine from $\text{RhClH}_2(\text{PPh}_3)_3$, whilst limited at room temperature, increases at higher hydrogenation temperatures:



- The initial coordination of the substrate is rate-limiting; however, the reductive elimination of the alkane is considered to be rapid:



- A potential ligand such as the nitrile present in a nitrile-butadiene copolymer may inhibit the catalytic hydrogenation cycle:



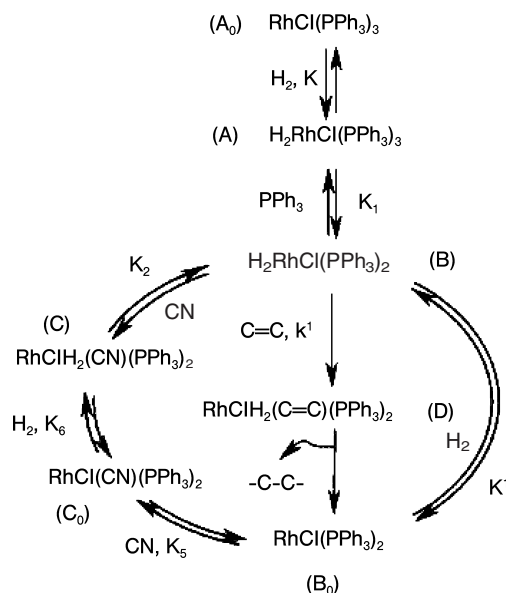
$[\text{Rh}(\text{CO})(\text{MeCN})(\text{PPh}_3)_2]\text{ClO}_4$ has been prepared [84] and $[\text{Rh}(\text{PPh}_3)_3(\text{MeCN})][\text{BF}_4]$ analyzed crystallographically by Pimblett et al. [85]. Schrock and Osborn [86] report that the use of acetonitrile as a solvent has a deleterious effect on the hydrogenation activity of $[\text{Rh}(\text{diene})(\text{PPh}_3)_2]\text{A}$ ($\text{A} = \text{ClO}_4, \text{BF}_4$ or PF_6). To date, a detailed study of the propensity of nitrile to associate with complexes derived from $\text{RhCl}(\text{PPh}_3)_3$ is lacking, although Ohtani, Yamagishi and Fujimoto [87] have presented some spectrophotometric data on the system. As nitrile likely coordinates by donation of its lone pair of electrons, it experiences little of the steric hindrance which affects coordination of the olefin. It may therefore compete effectively with olefin for coordination to coordinatively unsaturated metal complexes.

Based on the above reactions, an overall mechanism for the hydrogenation of NBR catalyzed by Wilkinson's catalyst was proposed (see Scheme 19.4), which is also applicable to the kinetic performance of the homogeneous hydrogenation of PB [88] and styrene-butadiene *copolymers* [89], where K_2 and K_5 vanish.

Based on Scheme 19.4, the following mathematical equation can be derived for calculating the hydrogenation rate:

$$R_{\text{H}} = \frac{k' K' K K_1 [\text{H}_2] [\text{Rh}] [\text{C}=\text{C}]}{K K_1 + K' [\text{PPh}_3] + K K' [\text{H}_2] [\text{PPh}_3] + K K_1 K' [\text{H}_2] + K K_1 K_5 [\text{CN}] + K K_1 K_2 K' [\text{H}_2] [\text{CN}]} \quad (7)$$

The investigated experimental ranges and experimental estimations of the kinetic parameters for various hydrogenation systems are listed in Table 19.2,



Scheme 19.4 The proposed reaction mechanism for the RhCl(PPh₃)₃/NBR system [90].

Table 19.2 Kinetic parameters for homogeneous hydrogenation of diene-based polymers.

Polymer (solvent)	K [mM ⁻¹]	K_1 [mM]	K' [mM ⁻¹]	K_2 [mM ⁻¹]	K_5 [mM ⁻¹]	k' [mMs ⁻¹]	E [kJ mol ⁻¹]	Reference
NBR (chlorobenzene)	∞	1.44	3.41×10^{-3}	3.98×10^{-2}	2.71×10^{-2}	1.19	73.5	81
NBR (butanone)	∞	0.198	0.276	6.5×10^{-2}	0	4.23×10^{-4}	87.3	83
1,4-PB (<i>o</i> -di- chlorobenzene)	0.60	4.45	0.59	0	0	1.28×10^{-3}	98.5	88
SBS (<i>o</i> -di- chlorobenzene)	0.31	3.13	0.63	0	0	3.26×10^{-4}	78.8	89
SB (toluene)	1.23	4.70	0.72	0	0	4.77×10^{-4}	60.8	89

with typical reaction conditions provided in Table 19.3. These parameters are consistent with the observed experimental results. For the hydrogenation of NBR in chlorobenzene using RhCl(PPh₃)₃, Bhattacharjee et al. [91] reported a value of 22 kJ mol⁻¹ for the apparent activation energy, though this was not consistent with the normal range of reaction activation energy and also quite different from the value shown in Table 19.2. However, these authors did not provide sufficient data to account for the discrepancy. It would appear from this value of activation energy that Bhattacharjee et al.'s catalytic hydrogenation study was possibly mass transfer-controlled.

Table 19.3 Typical reaction conditions for the hydrogenation of polybutadiene (PB), styrene-butadiene diblock copolymer (SB), styrene-butadiene-styrene tri-block copolymer (SBS) and nitrile butadiene rubber (NBR).

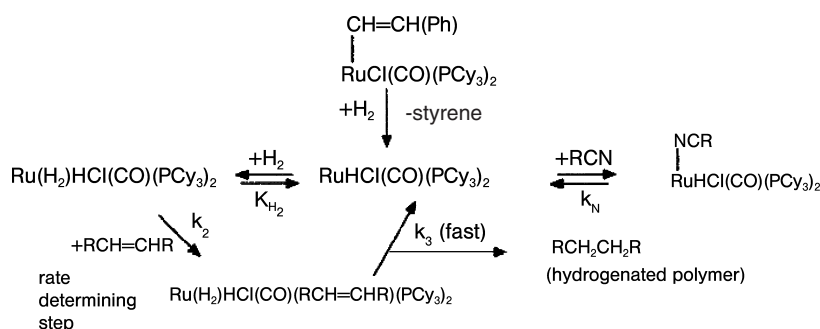
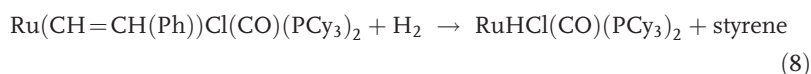
Polymer	[Rh] [mM]	[PPh ₃] [mM]	Temperature [K]	H ₂ [mM] (P _{H₂} [MPa])	Solvent	Reference
NBR	0.080	4.0	418.2	101 (2.37)	Chlorobenzene	81
NBR	1.958	0	313.2	3.142 (0.10)	Butanone	83
1,4-PB	1.99	7.40	338.2	3.90 (0.10)	<i>o</i> -Dichlorobenzene	88
SBS	1.99	7.40	338.2	3.90 (0.10)	<i>o</i> -Dichlorobenzene	89
SB	2.04	0	324.2	3.17 (0.10)	Toluene	89

19.2.2.2 Ruthenium-Based Catalysts

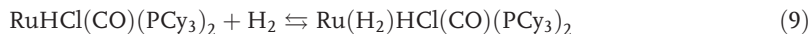
Ruthenium catalysts, such as Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂, have been found to be active for catalyzing the hydrogenation of various diene-based polymers. The catalytic mechanism for the hydrogenation of NBR, SBR and PB has been investigated [68].

Kinetic results show that the hydrogenation reaction rate exhibits a first-order dependence on both hydrogen concentration, [H₂], and the total ruthenium concentration, [Ru]_T and an inverse dependence on the nitrile concentration, [CN]. The catalytic mechanism proposed for polymer hydrogenation is illustrated in Scheme 19.5 and the main points of the mechanism are outlined below:

- Rapid hydrogenation of the styryl group in Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂, to give the active species RuHCl(CO)(PCy₃)₂, and styrene, which is subsequently rapidly hydrogenated to ethyl benzene.

**Scheme 19.5** Mechanism of nitrile butadiene rubber (NBR) hydrogenation catalyzed by Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂.

- The coordination of H_2 to $RuHCl(CO)(PCy_3)_2$ is the initial step in the catalytic cycle.



- The coordination of olefin before the final rapid elimination of products and regeneration of $RuHCl(CO)(PCy_3)_2$, which is assumed to be the rate-determining step:



- A potential ligand such as a nitrile may inhibit the hydrogenation cycle:



Based on the above reaction mechanism, and with some reasonable simplification, the hydrogenation rate can be expressed as:

$$R_H = \frac{k_1 [H_2] [Ru]_T [C=C]}{1 + K_N [RCN]} \quad (13)$$

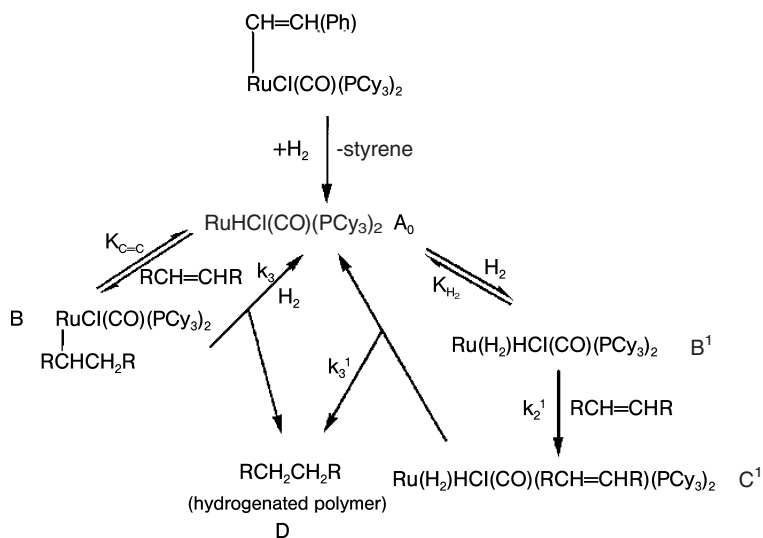
The mechanism for this catalyst for the hydrogenation of *cis*-1,4-polyisoprene (CPIP) is slightly different [69]. As there was no clear evidence that coordination of hydrogen occurs prior to the coordination of $C=C$ to the $RuHCl(CO)(PCy_3)_2$, there may be two possible pathways for the hydrogenation of CPIP in the presence of $Ru(CH=CH(Ph))Cl(CO)(PCy_3)_2$, namely an unsaturated path and a hydride path. The catalytic mechanism for these two pathways is represented in Scheme 19.6.

Based on this mechanism, if the unsaturated pathway ($A_0 \rightarrow B \rightarrow D$) is undertaken, with the reaction of the alkyl complex with hydrogen serving as the rate-limiting step, the hydrogenation rate can be expressed as:

$$R_H = \frac{k_3 K_{C=C} [H_2] [Ru]_T [C=C]}{1 + K_{C=C} [C=C]} \quad (14)$$

If the hydride pathway ($A_0 \rightarrow B' \rightarrow C' \rightarrow D$) is undertaken, the hydrogenation rate can be expressed as:

$$R_H = \frac{K_2 K_{H_2} [H_2] [Ru]_T [C=C]}{1 + K_{H_2} [H_2]} \quad (15)$$

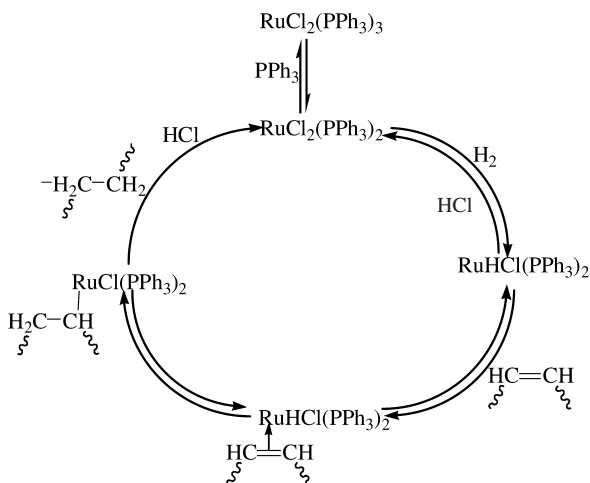


Scheme 19.6 Proposed mechanism of *cis*-1,4-polyisoprene (CPIP) hydrogenation using $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$.

If both K_{H_2} and $K_{\text{C}=\text{C}}$ are assumed to be very small, depending on which pathway is considered, then both equations will reduce to

$$R_{\text{H}} = k[\text{H}_2][\text{Ru}]_{\text{T}}[\text{C}=\text{C}] \quad (16)$$

which is consistent with the observed experimental kinetics.



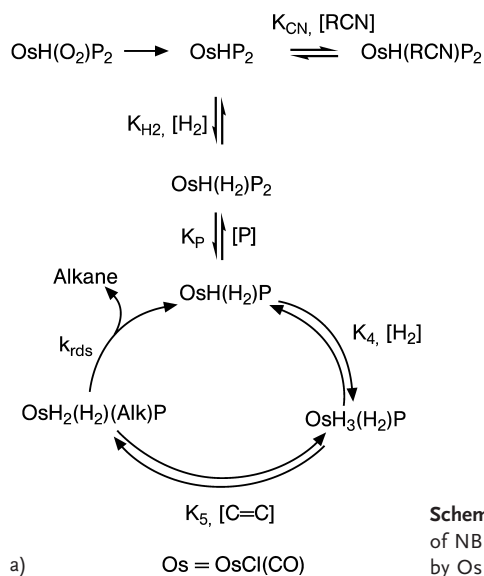
Scheme 19.7 Proposed mechanism for polybutadiene (PB) hydrogenation using $\text{RuCl}_2(\text{PPh}_3)_3$.

Rao et al. [70] investigated the hydrogenation of PB catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$, and showed a degree of hydrogenation >99% to be obtained within 6 h using 0.3 mol.% catalyst at 100°C and under 50 bar H_2 pressure. These authors proposed the possible mechanism shown in Scheme 19.7, but provided no detailed kinetic data to check the reliability of the above mechanism.

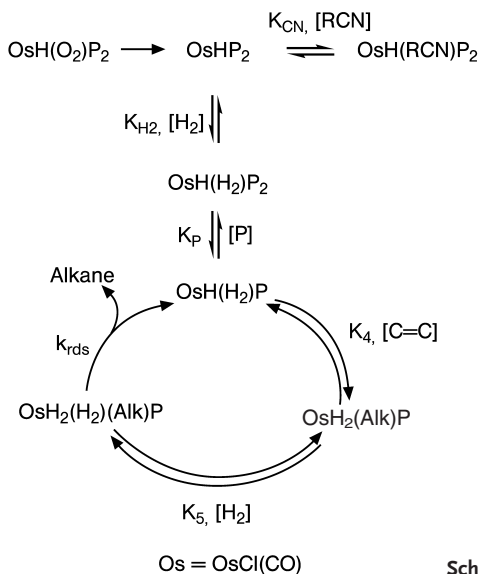
19.2.2.3 Osmium-Based Catalysts

For the hydrogenation of NBR, osmium complexes such as $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ have shown distinctive performance which permits their discrimination from Rh- and Ru-based catalysts [65]. A somewhat difficult element of the kinetic NBR hydrogenation data is the apparent second-to-zero-order dependence of the reaction rate with respect to $[\text{H}_2]$. A second-order behavior requires 2 molecules of H_2 either to produce an active complex or to participate in the rate-determining step. Bakhmutov et al. [92] identified an exchange between the apical hydride and the *trans*-coordinated dihydrogen ligand, but concluded that the trihydride could at most be a reactive intermediate. The addition of a second molecule of H_2 to the catalyst intermediate had not been observed. Another distinguishing characteristic in the Os catalytic system is that of severe inhibition of hydrogenation activity when additional PCy_3 is present. Based on these phenomena, two possible hydrogenation mechanisms have been proposed (Schemes 19.8a and b).

A rate expression, as shown in Eq. (17), may be obtained from Scheme 19.8a:



Scheme 19.8 (a, b) Alternative mechanisms of NBR hydrogenation catalyzed by $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$.



Scheme 19.8b

 $R_{\text{H}} =$

$$\frac{k_{\text{rds}} K_{\text{H}_2} K_{\text{P}} K_4 K_5 [\text{Os}]_{\text{T}} [\text{H}_2]^2 [\text{C}=\text{C}]}{[\text{P}] (1 + K_{\text{CN}} [\text{CN}] + K_{\text{H}_2} [\text{H}_2]) + K_{\text{H}_2} K_{\text{P}} [\text{H}_2] + K_{\text{H}_2} K_{\text{P}} K_4 [\text{H}_2]^2 (1 + K_5 [\text{C}=\text{C}])} \quad (17)$$

The rate expression is consistent with the observed kinetic data. A similar mechanism was also proposed for the hydrogenation of polyisoprene catalyzed by $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ [93].

Scheme 19.8b illustrates a more conventional mechanism, which results in a rate expression as shown in Eq. (18):

 $R_{\text{H}} =$

$$\frac{k_{\text{rds}} A [\text{Os}]_{\text{T}} [\text{H}_2]^2 [\text{C}=\text{C}]}{[\text{P}] (1 + K_{\text{CN}} [\text{CN}] + K_{\text{H}_2} [\text{H}_2]) + K_{\text{H}_2} K_{\text{P}} [\text{H}_2] + B [\text{C}=\text{C}] [\text{H}_2] (1 + C [\text{H}_2])} \quad (18)$$

While this mechanism involves lower formal coordination numbers than that of Scheme 19.8a, its shortcoming is a zero-order dependence on $[\text{H}_2]$ that must be accompanied by a zero-order reaction dependence on $[\text{C}=\text{C}]$.

19.2.2.4 Palladium Complexes

Palladium acetate has an unusual structure that comprises three palladium atoms in a triangular arrangement, held together by six bridging acetate groups. Details of the structure of the complex have been reported [75]. The catalyst has been used for the hydrogenation of both nitrile rubber and natural rubber [74–76].

Another palladium complex, namely, a six-membered cyclopalladate complex of 2-benzoyl pyridine, has also been used for the hydrogenation of polymers [77, 78]. Possible catalytic mechanisms for the hydrogenation of natural rubber [76] and NBR [77] catalyzed by these two complexes were proposed, but unfortunately the authors did not provide sufficient evidence to support their proposed mechanisms.

Although Ziegler-type catalysts have been widely investigated for the homogeneous hydrogenation of polymers, their catalytic mechanism remains unknown. One possible reason for this may be the complexity of the coordination catalysis and the instability of the catalysts. Metallocene catalysts are highly sensitive to impurities, and consequently it is very difficult to obtain reproducible experimental data providing reliable kinetic and mechanistic information.

19.2.3

Kinetic Mechanism Discrimination

Modeling and analysis of the kinetics represent powerful tools by which a better understanding of the catalysis involved in polymer hydrogenation may be obtained. These approaches also form the basis for a more thorough design of chemical reactors, and for a better insight into the behavior of existing reactors. In homogeneous catalytic systems, in the presence of organometallic catalysts, complicated equilibrium reaction cycles often exist and in general the networks composed of the elementary reactions are highly complex. Thus, model discrimination, selection on the basis of experiment of the best rate equation among a set of rivals, is very important. Fortunately, on the basis that overall catalytic intermediates can be considered to be reasonably constant, model discrimination may be significantly simplified, and a generalized method has quite recently been proposed for the hydrogenation of diene-based polymers [94].

19.3

Engineering Art

Homogeneous polymer hydrogenation operation involves a number of unit operations, and some typical procedures are shown in Figure 19.1 with respect to NBR hydrogenation. The major unit operations include homogeneous catalytic hydrogenation, catalyst recovery and solvent recycling, in addition to emulsion polymerization before the hydrogenation stage. Because of the high exothermicity in the initial stage of the hydrogenation reaction, and because gaseous hydrogen is used, heat transfer and mass transfer are major concerns for hydrogenation reactors. As a high degree of hydrogenation is usually required for high-performance hydrogenated elastomers, a suitable flow pattern in the reactor is also required for a continuous operation, besides a need for superior mass transfer and heat transfer. Because of the high price of the catalyst used, and also because of potential catalyst toxicity, catalyst recovery is a critical stage for

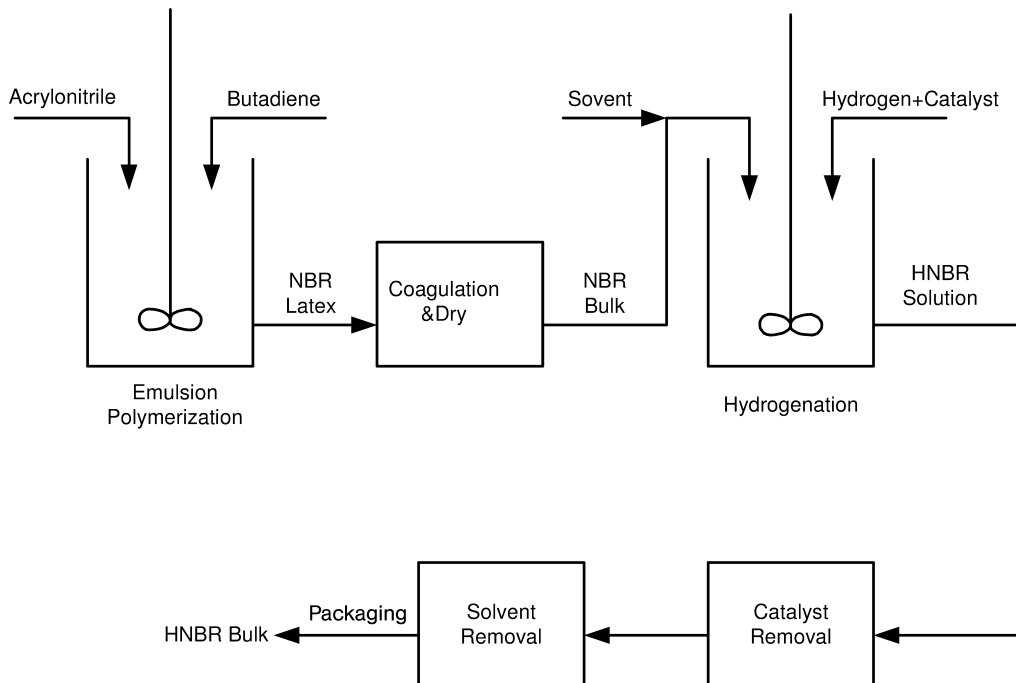


Fig. 19.1 Schematic process for the production of hydrogenated nitrile butadiene rubber (HNBR).

both batch and continuous operations. Likewise, as large amounts of organic solvent are required to realize homogeneous hydrogenation, an efficient design for solvent removal and recycle is necessary. Together, these three aspects determine the commercial feasibility of the hydrogenation process.

19.3.1

Catalyst Recovery

Catalyst recovery is a universal problem in the field of homogeneous catalysis. For the homogeneous hydrogenation of unsaturated polymers, the incentives of catalyst removal dwell on both improving the quality of the polymer product and on reducing the high costs of the process that relate mainly to the expensive noble metals often used as catalysts. Catalyst removal is especially difficult from polymer solutions because of the high viscosity and the good compatibility between the catalysts and the functionalized polymers. In general, two main methods are used for the removal of metal catalysts. The first method is to precipitate the catalyst from the polymer solution and then to separate it by filtration or gravity settling. The second method is to adsorb the catalyst from the polymer solution by ion-exchange resins or other absorbents which have an affinity for the spent catalyst.

19.3.1.1 Precipitation

Precipitation of the catalyst can be effected by treating the polymer solution with acid/base and/or oxidants. Poloso and Murray [95] proposed a method to recycle the nickel octanoate $((\text{CH}_3(\text{CH}_2)_6\text{CO}_2)_2\text{Ni})$ /triethylaluminum $((\text{C}_2\text{H}_5)_3\text{Al})$ catalyst from a styrene-butadiene polymer solution. The polymer solution containing the catalysts was refluxed with 4 wt.% glacial acetic acid (relative to polymer) for 4 h, followed by treatment with 1.4 wt.% anhydrous ammonia. The solution was then filtered through a diatomaceous earth. The nickel content in the polymer was decreased from 310 ppm to 5.6 ppm.

In a method developed by Kang [96], 2 equiv. dimethylglyoxime (based on nickel content) was used to treat a butadiene-styrene polymer solution. The reddish bis(dimethylglyoximate) nickel complex was precipitated and then removed by filtration. By using this method, the nickel content in the polymer was reduced to less than 1 ppm. Alternatively, Hoxmeier [97] mixed the polymer solution with azelaic acid or adipic acid (50 wt.% excess based on the metals) in organic solvents, after which a phase separation was realized by gravity settling. Subsequently, it was claimed that nickel levels within the polymers were reduced to 2 ppm. The process was later improved by using hydrogen peroxide to oxidize the nickel catalyst in the polymer solution initially, and then by adding azelaic acid or adipic acid as an aqueous solution to precipitate the catalyst [98]. Nickel-based catalysts have also been removed by contacting the polymer solution with molecular oxygen with subsequent treatment with activated carbon [99]. Other similar methods to precipitate catalysts from the polymer solutions include contacting the polymer solution with a trialkylaluminum compound in the presence of water [100], treating the polymer solution with a chelating resin which is comprised of iminodiacetate ions [101], bubbling oxygen/nitrogen in the presence of an aqueous solution of an acid [102], reacting with an aqueous solution of ammonia and carbon dioxide [103], and contacting with an aqueous solution of a weak acid followed by contacting with an aqueous solution of a weak base [104]. In selecting a suitable agent to remove metallic catalyst residues from hydrogenated polymer solutions, the following criteria should be considered: (i) the agent should be substantially inert toward the polymer and the polymer solvent; and (ii) it should be capable of turning the catalyst into an insoluble compound, efficiently. Contamination of the polymer by the catalyst recovery procedure must also be considered.

19.3.1.2 Adsorption

Adsorption is commonly used for catalyst removal/recovery. The process involves treating the polymer solution with suitable materials which adsorb the catalyst residue and are then removed by filtration. Panster et al. [105] proposed a method involving adsorbents made from organosiloxane copolycondensates to recover rhodium and ruthenium catalysts from solutions of HNBR. These authors claimed that the residual rhodium could be reduced to less than 5 ppm, based on the HNBR content which had a hydrogenation conversion of over

99%. Silicates, including calcium silicate, magnesium silicate and diatomaceous earth, have also been used as adsorbers [106]. When these were applied to a hydrogenated SBS solution containing a nickel-based catalyst, the nickel content of the polymer was reduced to less than 1 ppm. Rhodium-based catalyst residues from HNBR solution can also be removed by using an ion-exchange resin with thiourea functional groups present on a resin which is both macroporous and monodispersed [107]. The criterion for selecting adsorbers is similar to that for selecting a precipitating agent: an efficient catalyst adsorber should be inert to both the polymer and the solvent.

19.3.2

Solvent Recycling

Solvent recycling is an important post-treatment stage of the homogeneous catalytic hydrogenation of polymers, for both economical and environmental reasons. This topic has not been widely investigated for homogeneous polymer hydrogenation operations, but in present-day processes the organic solvents used are stripped by steam, which is itself an energy-intensive operation.

In other related areas, such as solution polymerization and bulk polymerization, the removal/recycling of solvents or unreacted monomer has been extensively investigated [108–112]. The methods used are based on lateral heat-dependent operations such as evaporation and steam-stripping, or non-lateral heat-dependent operations that include a variety of extraction procedures.

Many types of equipment have been developed to improve the evaporation of solvent in order to provide energy savings. The most widely used techniques for devolatilization are the falling strand devolatilizer (FSD), the thin-film evaporator and the vented extruder [113].

The FSD is a flash evaporator, whereby the preheated polymer solution/melt falls within the vessel primarily by gravity, while the volatiles evaporate during falling. This method is normally used with process streams that are not exceptionally temperature-sensitive and where the concentration of volatiles is relatively high.

Thin-film and surface renewal evaporators are mostly applied to materials with medium to high viscosity, or to high-boiling contaminated mixtures. A typical thin-film evaporator employs a unique rotor with an array of discrete, plow-like blades attached to the rotor core. The blades transport the viscous concentrate or melt through the evaporator while simultaneously forming films to facilitate heat and mass transfer.

Single-screw and double-screw extruders are normally used for polymer melts to accomplish the deaeration or devolatilization of residual volatiles. Devolatilization in an extruder is effected through formation of the venting zone inside the chamber by carefully designed upstream and downstream screw sections.

Many techniques have also been developed to improve devolatilization efficiency, including steam stripping [114], second fluid-assisted devolatilization [115], supercritical fluid devolatilization [116], and a variety of specially designed

devolatilizers. Some of the above methods can also be used for solvent recycling in polymer hydrogenation processes.

19.3.3

Reactor Technology and Catalytic Engineering Aspects

There are many commercial advantages to hydrogenating relatively inexpensive polymers in order to create new, more valuable materials. Polymer hydrogenation is not widely developed today on a commercial scale, however, mainly because of the high production costs associated with catalyst and reactor technologies. The development of an efficient reactor for homogeneous hydrogenation of diene-based polymers remains a major challenge for several reasons:

- In order to reduce production costs, high polymer concentrations are preferred in hydrogenation operations. However, the viscosity of polymer solutions rises rapidly as the polymer concentration increases. In present-day commercial processes, polymer concentrations do not normally exceed 15 wt.%.
- The hydrogenation operation involves hydrogen transfer from the gas phase into the viscous polymer solution phase. If the mass transfer capacity is not sufficiently superior, the hydrogenation could be significantly retarded and product quality adversely affected.
- The hydrogenation reaction is highly exothermic. Thus, heat release during the initial hydrogenation may be a serious problem, and a reactor with a superior heat transfer capacity tunability will be required.
- Due to the viscous and highly exothermic characteristics of the hydrogenation reactions, the reactor should have superior mixing capabilities in order to avoid possible crosslinking induced by hot spots in the reactor.
- As high hydrogenation conversion is usually desired, and crosslinking of the polymer should be avoided, correct control of the reaction conditions is very important.

Among present-day commercial processes for the homogeneous hydrogenation of polymers, a semi-batch operation system prevails where the hydrogen gas supply is provided continuously and the liquid phase is operated batchwise. A semi-batch operation is suitable for relatively small volume production, but it is not economical for high-production yields. Such semi-batch reactor systems cannot meet the needs of the growing demand for hydrogenated polymers, and the development of more efficient reactor systems is needed. A Japanese Patent [117] disclosed a production process for hydrogenated polymer wherein a polymer solution containing olefinic unsaturated groups, hydrogen gas, and a hydrogenation catalyst are continuously supplied to a stirred-tank reactor and the reaction product is continuously removed. Another Japanese Patent [118] disclosed a continuous production process of a hydrogenated polymer containing olefinic unsaturated groups wherein plural reactors are connected in series and hydrogen is supplied to at least one of the reactors from the lower portion

thereof. An improved method was proposed [119] to obtain a polymer having a desirable degree of hydrogenation steadily for a long period in the above continuous reactors by recycling one part of the hydrogenated polymer solution. Pan and Rempel et al. [120–122] investigated the effect of various reactor performances on the hydrogenation of diene-based polymers via modeling and simulation, and proposed that an optimal reactor for diene-based polymer hydrogenation would be a plug flow reactor with an instantaneous mixing component in the inlet zone. These studies provide useful information for commercial continuous hydrogenation process development.

19.4

A Commercial Example:

Production of HNBR via a Homogeneous Hydrogenation Route

HNBR has an intriguing combination of properties [123], including high tensile strength, low permanent set (especially at high temperatures), very good abrasion resistance and high elasticity. HNBR also shows excellent stability towards heat, being able to resist temperatures of up to ca. 150 °C (NBR under the same conditions is stable up to only ca. 120 °C); it also demonstrates better properties at low temperatures (lower brittle point) than other heat- and oil-resistant elastomers. This combination of properties is opening up a broad range of applications for these materials, particularly in the automotive industry. HNBR 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 rapeseed oil methyl ester. 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.

There are two major commercial producers of HNBR worldwide. Nippon Zeon Corporation manufactures HNBR (heterogeneous hydrogenation) under the tradename Zetpol[®], while Lanxess Inc. produces HNBR (homogeneous hydrogenation) in Orange, Texas, and in Leverkusen, Germany under the tradename Therban[®]. The manufacturing process of HNBR is shown schematically in Figure 19.1. The process begins with the production of an emulsion-polymerized NBR which is then dissolved in an appropriate solvent (chlorobenzene). When dissolution is complete, the addition of hydrogen gas, in conjunction with a precious-metal catalyst at a designated temperature and pressure, brings about a selective hydrogenation to produce the hydrogenated polymer. The solvent and catalyst are then recovered and the remaining polymer crumb is dried. After vulcanization, the HNBR is ready for industrial use.

19.5

Future Outlook and Perspectives

Hydrogenated polymers have many desirable properties over their parent polymers, although the high cost of hydrogenated products still restricts their widespread application. The following aspects should be considered for the sustainable development of the hydrogenated polymer industry:

- The development of highly efficient and easily recoverable catalyst systems. Today, the high cost of hydrogenated polymers is due mainly to the cost of the metal catalyst and its recovery operation.
- A reduction in the amounts of organic solvent used in the hydrogenation process. Considerable energy costs result from solvent recycling. Investigations into the hydrogenation of NBR in supercritical fluid media have been carried out, and positive results obtained [124, 125]. Considerable cost savings could be realized if an efficient catalyst system were to be developed for the hydrogenation of polymers in aqueous latex form [126, 127].
- The development of high-efficiency reactors (e.g., continuous/flexible systems) for the hydrogenation process [117–122].
- The extension of new applications for hydrogenated polymers.
- An overall improvement on the hydrogenation process to reduce production costs is required.

Abbreviations

CPIP	<i>cis</i> -1,4-polyisoprene
FSD	falling strand devolatilizer
HNBR	hydrogenated nitrile butadiene rubber
NBR	acrylonitrile-butadiene rubber
PB	polybutadiene
SBR	styrene-butadiene rubber
SBS	styrene-butadiene-styrene triblock copolymer
SIS	styrene-isoprene-styrene triblock copolymer
XNBR	carboxylated nitrile rubber

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