HYDROGENATION OF DEPROTEINIZED NATURAL RUBBER LATEX

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Thesis

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HYDROGENATION OF DEPROTEINIZED NATURAL RUBBER LATEX

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ABSTRACT

Natural rubber (NR), generally, degrades when exposed to sunlight, ozone, and oxygen due to the unsaturation of carbon-carbon double bonds within the isoprene backbone. Hydrogenation reaction is a chemical modification method commonly used to improve the polymer properties to desirable physical and chemical properties. In the past, most hydrogenation reactions were carried out in solution form of rubber. However, NR and certain synthetic elastomers are available in the form of aqueous latex or emulsion, thus it is advantageous to hydrogenate the elastomer in the latex phase. There are three possible ways to hydrogenate elastomers in latex form, namely by homogeneous, heterogeneous and non-catalytic hydrogenations.

Thus, this research studied the homogeneous catalytic hydrogenation of deproteinized natural rubber (DPNR) latex using palladium acetate ($Pd(OAc)_2$) as a catalyst, and investigated the effect of dry rubber content (DRC) of DPNR latex, ratio (catalyst/rubber), hydrogen pressure, reaction temperature, and reaction time. The optimum condition is achieved using DPNR latex at 10 DRC in the presence of ration (catalyst/rubber) 0.0600 at 50°C under 3 MPa H_2 pressure for 6 h.

For structural characterization, the obtained hydrogenated DPNR (HDPNR) showed a characteristic band at 735 cm^{-1} with respect to $-CH_2-$ group of saturated unit of HDPNR from Fourier transform infrared (FT-IR) spectroscopic investigation. ^{1}H-NMR spectrum showed the signal at 0.8 and 1.2 ppm, which are assigned to $-CH_3$ and $-CH_2-$ and the ^{13}C-NMR showed the signal at 32.37, 32.74, 24.44 and 19.69, which are assigned to $-C_{\alpha\gamma}-$,-CH-, $-C_{\beta\beta}-$ and $-CH_3$ carbon of saturated unit, respectively. Thermal behaviors of the HDPNR characterized by Different Scanning Carolimetry showed that the glass transition temperatures (T_g) of the HDPNR at 75 percentage of hydrogenation did not appreciably affect Tg. Consequently, the hydrogenated rubber product still had a high rubbery property.

KEY WORDS: HYDROGENATION/ DE-PROTEINIZED NATURAL RUBBER (DPNR)/ $Pd(OAc)_2$/ MODIFICATION OF RUBBER

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บทคัดย่อ

ยางธรรมชาติจะเกิดปฏิกิริยาย่อยสลายได้ง่ายมากเมื่อถูกแสงแดด โอโซน และออกซิเจน เนื่องจากโครงสร้างที่ไม่อิ่มตัวที่อยู่ในสายโซ่หลักของไอโซพรีน ปฏิกิริยาการเติมไฮโดรเจน จึงนับเป็นวิธีหนึ่งที่สำคัญที่ใช้ในการปรับปรุงสมบัติทางกายภาพ และเคมีของโพลิเมอร์ที่ไม่อิ่มตัว ให้มีความทนต่อการสลายตัวด้วยความร้อน แสงได้ดีขึ้น ปฏิกิริยาการเติมไฮโดรเจนในรูปของมี 3 วิธีคือ ปฏิกิริยาการเติมไฮโดรเจนโดยการใช้สารเร่งปฏิกิริยาที่รวมเป็นเนื้อเดียว (Homogeneous hydrogenation) ปฏิกิริยาการเติมไฮโดรเจนโดยการใช้สารเร่งปฏิกิริยาที่ไม่รวมเป็นเนื้อเดียว (Heterogeneous hydrogenation) และปฏิกิริยาการเติมไฮโดรเจนโดยไม่ใช้โดยไม่ใช้สารเร่งปฏิกริยา (noncatalytic hydrogenation) และได้มีรายงานกล่าวไว้ว่าสามารถเตรียมน้ำยางธรรมชาติที่ผ่านกระบวนการการเติมก๊าซไฮโดรเจน แต่โดยส่วนมากแล้วเป็นการทำปฏิกิริยาในรูปของสารละลาย แต่โดยธรรมชาติของยางธรรมชาติมักอยู่ในรูปของเหลว ดังนั้นงานวิจัยนี้จึงได้ศึกษาปฏิกิริยาการเติมไฮโดรเจนของน้ำยางธรรมชาติที่ผ่านการกำจัดโปรตีน (Deproteinized natural rubber) โดยใช้แพลเลเดียม อะซิเตต ($Pd(OAc)_2$) เป็นตัวเร่งปฏิกิริยา นอกจากนี้ยังได้ศึกษาผลของ ความเข้มข้นของน้ำยางธรรมชาติที่ผ่านการกำจัดโปรตีน (Dry rubber content) ความเข้มข้นของตัวเร่งปฏิกิริยา ความดันไฮโดรเจน อุณหภูมิ และ เวลาที่ใช้ในการเกิดปฏิกิริยา จากผลการทดลอง พบว่าเมื่อนำน้ำยาง DPNR ที่มีค่าอัตราส่วนระหว่างตัวเร่งปฏิกิริยากับเนื้อยางที่ 0.0600 ภายใต้ความดันก๊าซไฮโดรเจน 3 MPa ที่อุณหภูมิ 50 องศาเซลเซียส เป็นเวลา 6 ชั่วโมง ทำให้ได้น้ำยางที่ผ่านการเติมไฮโดรเจน 81.7% และพบว่าจาก FT-IR spectrum ปรากฏตำแหน่งของหมู่ $-CH_2-$ ที่ตำแหน่ง 735 cm^{-1} นอกจากนั้นการวิเคราะหีโครงสร้างโดยใช้ ^1H-NMR พบสัญญาณที่ 0.8 และ 1.2 ppm ซึ่งเป็นสัญญาณของ methyl และ methylene protons ของโครงสร้างที่อิ่มตัวของไอโซพรีน และจาก ^{13}C-NMR พบสัญญาณที่ 32.37, 32.74, 24.44 และ 19.69 ซึ่งเป็นสัญญาณของ methylene, methane, methylene และ methyl carbon ของโครงสร้างที่อิ่มตัวของไอโซพรีน จากผลที่กล่าวมาข้างต้นสามารถกล่าวได้ว่า เกิดปฏิกิริยาการผ่านไฮโดรเจนขึ้นจริง นอกจากนี้ได้ทำการศึกษาการทนต่อความร้อน จาก DSC พบว่าน้ำยางที่ผ่านการเติมไฮโดรเจน75% ไม่มีการเปลี่ยนแปลงอุณหภูมิของการเกิดเปลี่ยนเป็นสภาพคล้ายแก้ว

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LIST OF ABBREVIATIONS

BR = Butadiene rubber
cm^{-1} = Wavenumber
CR = Chloroprene rubber
°C = Degree celcius
DMG = Dimethylglyoxime
DPNR = Deproteinized natural rubber
DRC = Dry rubber content
DSC = Differential scanning calorimetry
ENR = Epoxidized natural rubber
EPDM = Ethylene propylene diene rubber
FL = Fresh latex
FTIR = Fourier transform infrared
g = Gram
GPC = Gel permeation chromatography
h = Hour
MH_z = Megahertz
HDPNR = Hydrogenated deproteinized natural rubber
HNBR = Hydrogenated nitrile rubber
IR = Synthetic polyisoprene
k = Rate constant
L = Liter
LRP = Large rubber particle
M = Molar
min = Minute
ml = Milliliter
mg = Milligram
mmol = Millimole
μm = Micrometer

LIST OF ABBREVIATIONS (Continued)

M_n = Number-average molecular-weight
M_w = Weight-average molecular-weight
MW = Molecular weight
MWD = Molecular weight distribution
nm = Nanometer
NBR = Nitrile rubber
NMR = Nuclear magnetic resonance
NR = Natural rubber
MPa = Megapascal
$Pd(OAc)_2$ = Palladium (II) acetate
PEG = Polyethylene glycol
ppm = Part per million
psi = pound per square inch
PVP = Polyvinylpyrrolidone
$RhCl(PPh_3)_3$ = tris-triphenylphosphinechloro rhodium (I)
rpm = Round per minute
s = Second
SBR = Styrene butadiene rubber
SDS = Sodium dodecyl sulphate
SEC = Size exclusion chromatography
SRP = Small rubber particle
TMS = Tetramethylsilane
THF = Tetrahydrofuran
TEAL = Triethylaluminum
T_g = Glass transition temperature
TGA = Thermogravimetric analysis
TSH = *p*-toluenesulphonylhadrazide
(w/v) = Weight by volume

CHAPTER I

INTRODUCTION

Natural rubber (NR) latex is produced from rubber trees of which the dominant species is *Hevea Brasiliensis*. NR is largely composed of 94% rubber hydrocarbon (*cis*-1,4-polyisoprene) and 6% non-rubber components such as proteins, lipids, carbohydrates, inorganic constituents, *etc*. [1]. The high resilience, tear resistance, excellent dynamic properties, and fatique resistance are main advantages of natural rubber believed to result from proteins in the rubber structure [2]. Because of the unsaturation of carbon-carbon double bonds within the isoprene backbone, natural rubber is subject to degradation when exposed to sunlight, ozone, and oxygen. Chemical modification of natural rubber has been an active field of research because of the technological importance of the modified products.

Hydrogenation is a chemical modification method commonly used to improve polymer properties to desirable physical and chemical properties. It has been the most widely used process to modify not only properties but also the structures of dienic base polymers since they have reactive groups which resemble as that of polyalkenes.

In the previous works, the most hydrogenation reactions are carried out in solution form of rubber. However, NR and certain synthetic elastomers are available in the form of aqueous latex or emulsion, thus it would be advantageous to hydrogenate the elastomer in the latex phase. There are three possible ways to hydrogenate elastomers in latex form: hydrogenation of latex via a catalytic method using a cosolvent, using a water soluble catalyst or by a noncatalytic process [3]. In addition, a noncatalytic process technique, using diimide generated from the reaction between hydrazine hydrate and hydrogen peroxide, has also been found to efficiently hydrogenate NBR [4] and SBR [5]. However, a high level of gel occurred in these reactions. There is reported the hydrogenation of NBR in the presence of a water soluble catalyst, $RhCl(DPM)_3$, (DPM, diphenyl phosphino benzene *m*-sulfonate) [6]. It was found that hydrogenation of NBR up to 60% at 75°C under 1 atm of hydrogen was achieved in 12 h. Diimide generated *in situ* from *p*-toluenesulfonylhydrazide (TSH) [7] has also been used for hydrogenation of a diene polymer. Nevertheless, the reaction of polyisoprene with TSH at 140°C could only produce a low level of hydrogenation (<40% conversion), despite the use of a large amount of TSH. Inaddition, the polymer was partially *cis*-*trans* isomerized, depolymerized, and cyclized.

Because of the disadvantages of noncatalytic method, catalytic hydrogenation has been increasingly studied. Heterogeneous catalysts such as $Pd/CaCO_3$ can be used as catalysts for the hydrogenation of polymers [8]. Although heterogeneous catalysts do not have the problem of residue metal removal, a mass-transfer limitation is the main disadvantage in limiting their catalytic activity. Thus, the process requires the use of a high catalyst concentration and a long reaction time to obtain the desired level of hydrogenation. Homogeneous catalysts are favorable as catalysts for the hydrogenation of unsaturated polymers with or without sensitive functional group such as –CN or COOH because of their higher selectivity and absence of macroscopic diffusion

This present work has focused on the homogeneous catalytic hydrogenation process of deproteinized natural rubber (DPNR) using Palladium (II) acetate $Pd(OAc)_2$ as a catalyst and including the method to prepare the catalyst solution laboratory. $Pd(OAc)_2$ is monomeric in benzene at 80°C but crystallizes as the trimer, consisting of an equilateral triangle of Pd atoms each pair of which is bridged with two acetate groups in a butterfly conformation. Each metal atom achieves approximate square planar co-ordination. $Pd(OAc)_2$ acts as a catalyst for many organic reactions by combining with many common classes of organic compounds such as alkenes, dienes, and alkyl, aryl, and vinyl halides to form reactive adducts. The effect of %dry rubber content (DRC) of DPNR, catalyst concentration, hydrogen pressure, reaction temperature, and reaction time were also investigated.

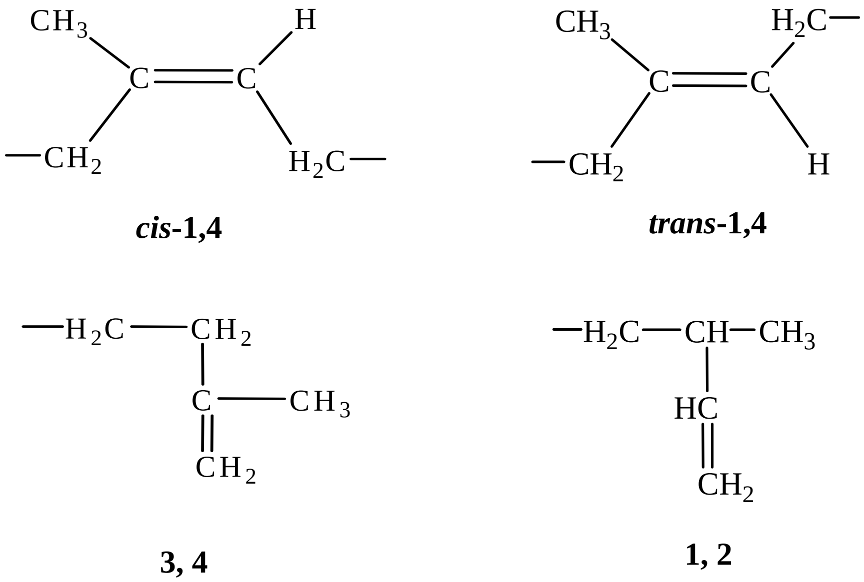
The hydrogenated DPNR is expected to show the improvement of physical properties comparable to ethylene propylene diene rubber (EPDM) and to have an excellent heat resistance, oxidation resistance, ozone resistance, and weathering aging.

CHAPTER II
LITERATURE REVIEW

2.1 Natural Rubber

2.1.1 Characteristics of Natural Rubber

Rubber from *Hevea brasiliensis* termed natural rubber (NR) is a high molecular-weight hydrocarbon, mainly composed of isoprene units, C_5H_8, liked to head-to-tail in the *cis* configuration, known as *cis*-1,4-polyisoprene. In the early stage of X-ray diffraction studies the double bonds in *Hevea* rubber are found to be in the *cis*-configuration [9, 10]. A wild polyisoprene called gutta percha is different from NR, in which the isoprene units are showed to be in the *trans*-configuration. Gutta percha is a typical crystalline polymer showing physical properties different from the rubber from *H. brasiliensis*. On the other hand, synthetic *cis*-1,4-polyisoprene prepared with a Ti-Al coordination catalyst (Ziegler catalyst) showed fundamental physical properties such as molecular weight, glass transition temperature, and melting point similar to NR. The isoprene units in Ti-Al catalyzed synthetic polyisoprene was found to be 98-99% *cis*-1,4, 0.3-1% 3,4 and 0.0-0.7% *trans*-1,4 units [11]. Here, the isomeric structure of isoprene units in Ti-Al catalyzed synthetic polyisoprene is shown in **Figure 2.1**. Usually, polyisoprene is a copolymer composed of these four isomeric units, although the 1,2 unit is generally a minor component. In spite of the remembrance of chemical structure, Ti-Al catalyzed synthetic polyisoprene was found to show properties different from NR as green rubber and cured rubber less than those of NR [12]. The presence of 3,4-isoprene units has been considered to be responsible for considerable differences between NR and synthetic *cis*-1,4 polyisoprene in processability, mechanical and physical properties as elastomer. However, it is reasonable to expect that the physical properties of polyisoprenes are affected by the distribution of the isomeric structure units along the polymer chain as well as the composition of the polymer. NR is consisted exclusively of



***cis*-1,4**

***trans*-1,4**

3, 4

1, 2

Figure 2.1 Isomeric structure of isoprene units

the *cis*-1,4 structure, while synthetic polyisoprenes synthesized by Zigler or lithium initiator contain 1-4% of the 3,4 structure. It is noteworthy that even the presence of very small amounts of the 3,4 units, it can interupt the crystallization on stretching that brings about tensile strength lower than that of NR for vulcanized rubber [13]. In addition, non-rubber components in NR, as shown in **Table 2.1**, such as proteins, have been believed to bring about properties characteristic of NR.

Table 2.1 Composition of solid natural rubber [14]

Component	**Percentage**
Rubber hydrocarbon	93.7
Neutral lipids	2.4
Glycolipids and Phospholipids	1.0
Proteins	2.2
Carbohydrates	0.4
Ash	0.2
Others	0.1

Practically, it is commonly accepted that synthetic *cis*-1,4-polyisoprene can not be substituted for NR in some applications which requires high elasticity, high tensile strength, and minimal heat built-up product.

NR is the most practically representative *cis*-1,4-polyisoprene accounting for more than 99% of the world's naturally rubbery source due to its high productivity of plant and excellent physical properties of rubber [15, 16]. NR is used in variable applications such as surgical gloves, tires and bridge bearing. The products from NR latex have distinct advantages over those which process from dry rubber; for example, better aging resistance, higher tensile strength and more consistent physical properties [15]. These advantages combined with the inherent properties of dry rubber, provided a material that can be molded, dipped or laminated to get a variety of specialty products. However, NR possesses some disadvantages over synthetic rubbers due to inconsistency of the porperties inherent in natural products.

It was reported that solid NR consists of about 94% rubber hydrocarbon and 6% non-rubber components such as lipids, proteins, sugars, etc [17]. These non-rubber components have been considered to play important roles for bringing about outstanding properties of NR [15]. Proteins in NR have believed to be an essential component controlling the properties of NR, especially cured rubber properties [18]. It has been regarded as a reactive substance to produce branching by the reaction with the abnormal group [19]. However, it was confirmed that proteins are not participated in the fundamental properties of NR [20]. On the contrary, proteins in NR were found to be a big disadvantage of NR due to thir allergenic character. It was reported that rubber products from NR latex, especially rubber gloves, caused Type I immediate hypersensitivity allergic reaction, which sometime resulted in anaphylaxis [21, 22]. FDA issued shern warning to the Type I allergic reaction caused by extractable proteins in latex-products and recommended to remove proteins or to protect the surface of latex-product not to elute proteins [23]. A new method was developed fro deproteinization of NR latex by the use of a proteolytic enzyme together with surfactant, which enable to reduce the nitrogen content in the resulting NR less than 0.02% [20, 24]. The residual nitrogenous compound was believed to be oligopeptide linked to rubber molecules, not residual proteins [24].

These non-rubber components, proteins and lipids are accompanied with polyisoprene from the starting point of biosynthesis to the final stage of rubber production as colloidal particles stabilized with lipid and protein layers.

The formation of natural rubber was presumed to start from dimethyl diphosphate (DMADP), although attempts to prove the incorporation of DMADP into rubber chain were unsuccessful [25, 26]. Chain extension was expected to proceed by successive condensation of isopentenyl diphosphate (IDP) to DMADP in the *cis*-configuration on the surface of rubber particles in latex form. According to the presumed steps of rubber formation, natural polyisoprenes should contain a dimethylallyl group at the initiating end, which is referred to ω-terminal, and diphosphate groups or hydroxyl group formed after dephosphorylation at the terminating end, which is referred to α-terminal.

Polyprenols consisting of isoprene between 9 and 23 units, have the expected strycture of both terminal groups. However, polyprenol consisting of only *cis*-isoprene units has not been ever found. Polyprenols have been classified into three groups: all-*trans* type such as solanesol; two-*trans* and poly-*cis* type such as bactoprenol and betulaprenol; and three-*trans* and poly-*cis* type such as ficaprenol [27].

Natural rubber from *Hevea brasiliensis* was also found to contain two *trans*-isoprene units per molecule. However, the dimethylallyl group and hydroxyl terminal groups, which are expected to form from the mechanism of rubber biosynthesis, were not identified as shown in **Figure 2.2** [28].

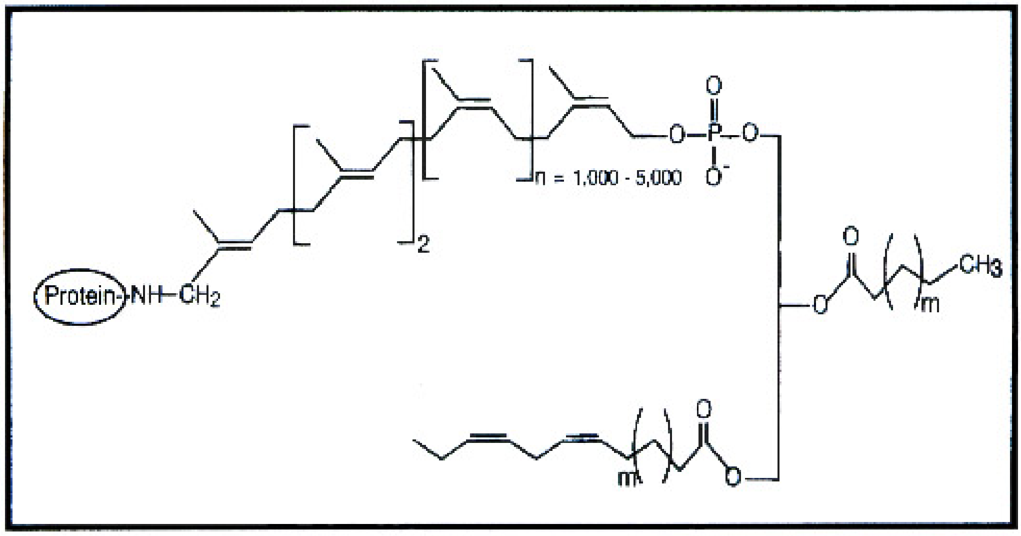


Figure 2.2 Presumed structure of *Hevea brasiliensis* [28]

In 1993, it was disclosed that *Hevea* rubber contains long-chain fatty acid groups linked to the rubber molecule though ester linkage of some lipid, which are possibly phospholipids [29]. These fatty acid groups were presumed to give the prominent physical properties characteristic of natural rubber by inducing rapid crystallization of polyisoprene chains [30]. Both terminal groups were presumed to act as an important role in the formation of branch points and crosslinking structure in natural rubber, which are different from the synthetic one.

2.1.2 Stability of natural rubber latex

The rubber hydrocarbon in fresh *Hevea* latex is predominantly cis-1,4 polyisoprene. The soluble fraction has typically a number-average molecular weight of about 300,000. The results of X-ray diffraction studies of crystallized natural rubber are consistent with a repeat distance corresponding to a predominantly *cis*-configuration about the double bond. Phospholipids (*ca* 2%) are strongly adsorbed to the surfaces of the rubber particles, and are thought to be intermediaries by which the protein are anchored on the rubber particles [31], as shown in **Figure 1.3**

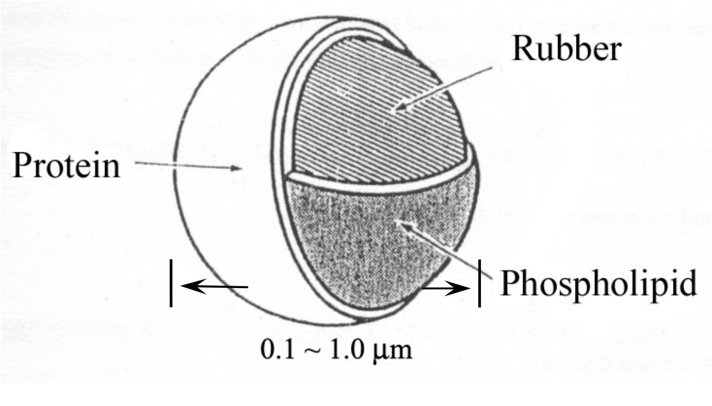


Figure 2.3 Schematic representation of rubber particle

2.1.3 Particle size of natural rubber

The particle size of rubber particles in the fresh field latex depends on the age and clone of rubber trees. Natural rubber latex from the mature trees was found to contain large and small rubber particles. The average size of large rubber particles (LRP) was about 0.04 – 4 μm with mean diameter of 1.03 μm. On the other hand, the size distributions of small rubber particles (SRP) in the serum phase ranging between 0.05 – 0.3 mm. The total latex shows a similar particle size distribution to that of the LRP rubber as can be seen from Figure 1.4 [32].

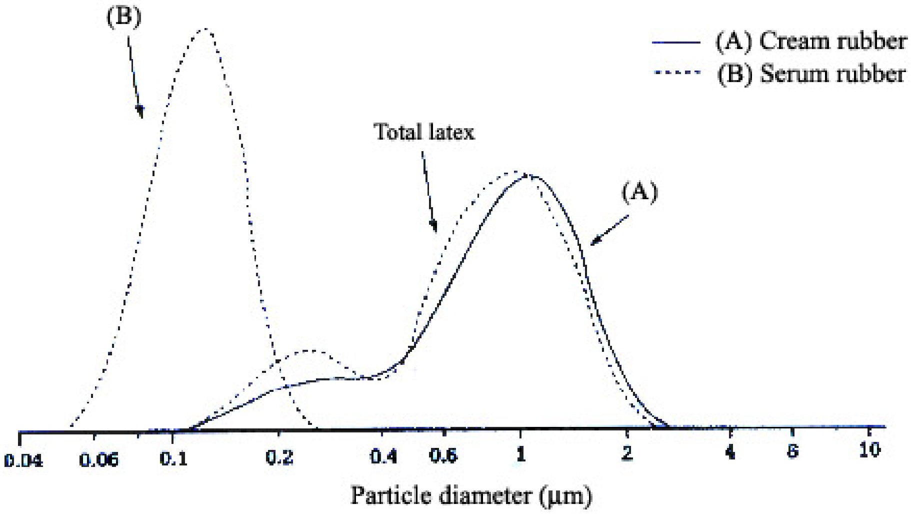


Figure 2.4 Particle size distribution of fresh field latex.

2.1.4 Molecular weight (MW) and molecular-weight distribution (MWD) of natural rubber from *Hevea brasiliensis*

NR obtained from *Hevea bransiliensis* is a polymer of a very high molecular-weight and wide MWD. The variation of MWD depends on the clone from which the rubber is obtained, the age of tree, soil and climatic conditions. It was reported that NR have a bimodal distribution. Exhausive studies of the MWD of NR in FL-latex by the use of size exclusion chromatography (SEC or GPC) was reported by

Subramaniam [33]. The distribution of all clonal rubbers can be classified into one of three types as shown in **Figure 2.5**.

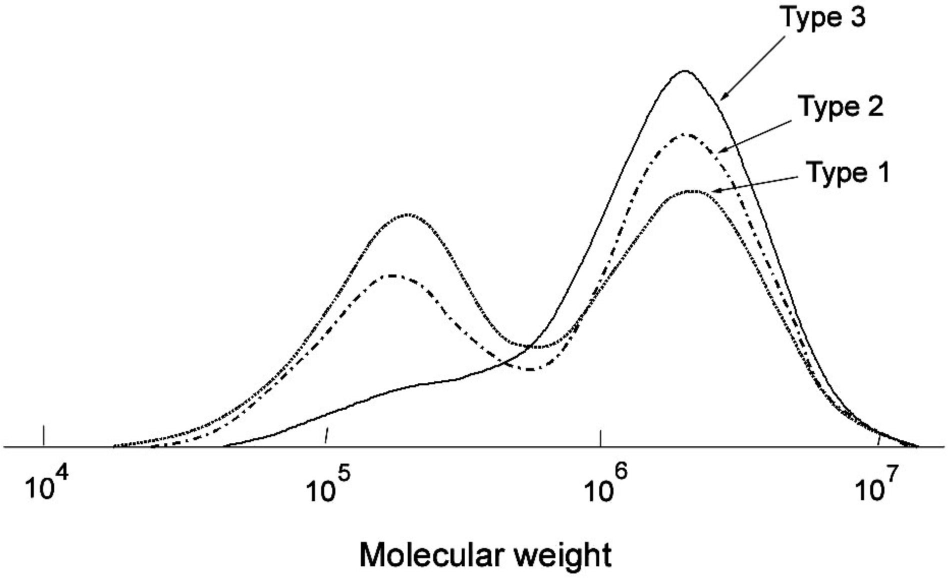


Figure 2.5 Types of molecular-weight distribution curves of natural rubber [33].

Type 1. Distinctly bimodal distribution where the peak height in the low molecular-weight region is nearly equal or slightly less than the peak height at the high molecular-weight region.

Type 2. Bimodal distribution where the height of the low molecular-weight peak is only half or less than the height of the high molecular-weight peak.

Type 3. Skewed unimodal distribution with a “shoulder” or a “plateau” in the low molecular-weight region.

The polydispersity of molecular-weight by the M_w/M_n value is extremely high in NR ranging from 2.5 to 10. The range of molecular weight is approximately the same in rubber from all clones, although the shapes of MWD curve are different, usually from about 3×10^4 to 1.2×10^7. The high molecular-weight peak appears between 1×10^6 and 2.5×10^6 for different rubbers. The peak top of the low molecular-weight peak is appeared between 1×10^5 and 2×10^5.

The high molecular-weight rubber fraction has been presumed to be derived from branching, presumably formed by the reaction of abnormal groups [34].

It has been inferred this bimodal distribution results from branching, with the high molecular-weight fraction presumably to have tri- or tetra-functional branch-points [34, 35]. The number of branch points increased with increasing the M_r value of fractionated rubbers. By extrapolation of this plot, it was postulated that the low molecular-weight rubber fraction consists of linear molecules, while the high molecular-weight rubber fraction comprises of branched rubber molecules [34]. It is conspicuous that the bimodal MWD of NR was retained even if all branch points and insoluble fraction were decomposed by deproteinization and transesterification or saponification of NR. This fact suggests that the bimodal MWD is implicited in the mechanism of rubber biosynthesis [36]. It is remarkable that this bimodal distribution can be observed for the rubber from *Hevea* seedlings, the low molecular-weight rubber, of one-month to three-years tree-age, as seen in **Figure 2.6** [37].

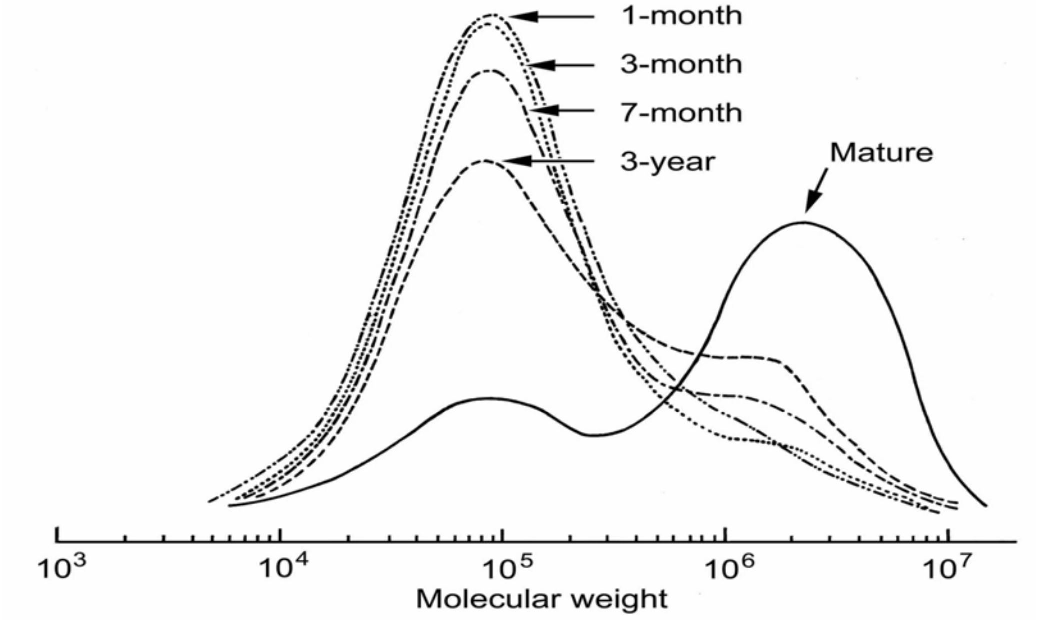


Figure 2.6 Molecular-weight distribution of NR from *Hevea* tree of different ages [41].

It can be seen from this figure that the molecular weight of these seedling rubbers was about one-tenth of that of mature tree and increased with increasing the age of the tree. Similarly, the ratio of low to high molecular-weight peaks decreased when the tree-aged increased. However, the peak position of high and low molecular-weight peaks was identical with that of the rubber obtained from mature three as well as that of ordinary NR. These findings imply that the bimodal MWD is predominantly derived from the rubber biosynthesis and not due to simple branching of rubber molecules. The relative intensity of the high molecular-weight peaks and M_n reduced by *ca* 40% after tranesterification as shown in **Table 2.2**. This indicats that a part of the high molecular-weight rubber is acquired from branching formation.

Table 2.2 Molecular weight of rubber obtained from *Hevea* seedlings of different ages, determined by GPC and osmometry

Age of plant	GPC			Osmometry
	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	M_w/M_n	$M_n \times 10^{-5}$
1-month	2.7	6.6	4.1	1.1
3-month	2.9 (2.1)[a]	6.1 (6.0)	4.8 (3.5)	1.4 (0.87)
7-month	4.4 (3.0)	7.3 (7.1)	6.0 (4.2)	1.9 (0.94)
3-year	4.5 (3.5)	7.3 (7.2)	6.2 (4.9)	2.9 (1.2)
17-year (mature)	25 (19)	27 (18)	9.3 (10.6)	12 (10)
Low M_r fraction[b]	1.3	8.1	1.6	1.0

[a] Values in parentheses are molecular weight after transesterification.

[b] Obtained from rubber of 17-year-old tree.

It is believed that the particle size of rubber in latex is an important factor influencing the biosynthesis mechanisms controlling molecular weight of NR. In 1980, it was reported that there was no relationship between the mean particle size diameters, measured by soap absorption method, and molecular weight of rubbers from several clones [38]. However, Subramaniam [39] and Yeang *et al.* [40] reported that the small rubber particles contain rubber of very high molecular-weight. Recently, small rubber particle (SRP) separating from the serum fraction, which is obtained by centrifugation of FL-latex, was found to consist of rubber molecules showing a unimodal MWD. On the contrary, the large rubber particle (LRP) obtaining from the cream fraction of centrifuged FL-latex showed the bimodal MWD [41]. The unimodal peak-top value of rubber in SRP fell down between the two peak values of the bimodal MWD observed in rubber from LRP as illustrated in **Figure** 2.7. The M_n value of SRP obtained by osmometry was higher than that of LRP, while there was no significant difference in the M_w obtained by light scattering measurement.

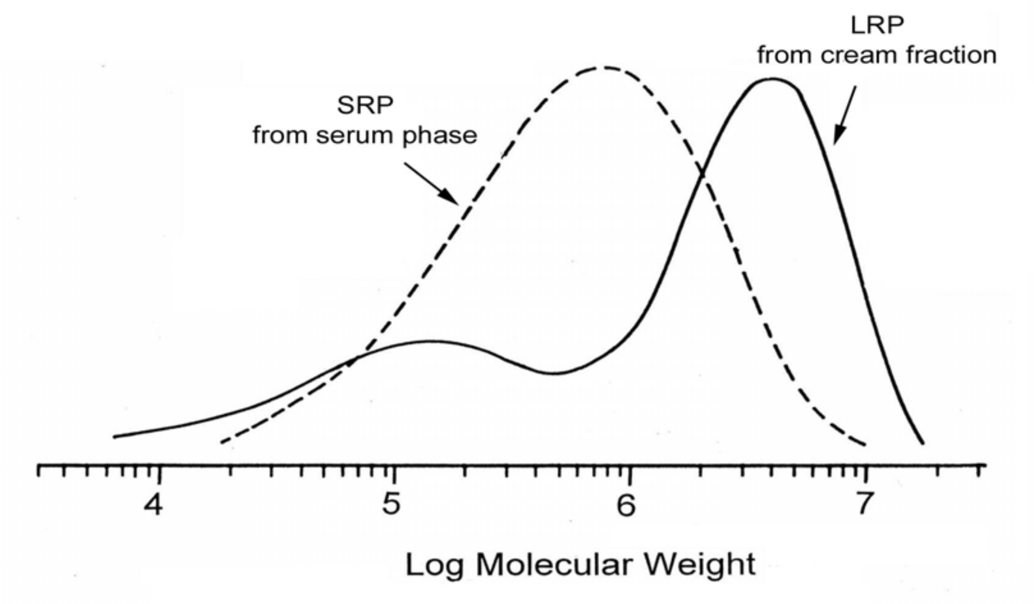


Figure 2.7 Molecular-weight distribution of rubber from small rubber particles and large rubber particle in FL-latex [41].

As mentioned above, the MWD of rubber particles obtained from seedlings contained low molecular-weight rubber having average particle size of 0.1 μm, which showed a unimodal distribution with a peak top at 1×10^5. The structure of this rubber is similar to that observed for the LRP from mature *Hevea* tree, in which the rubber molecule is functionalized with phospholipid comprising branch-points, while that in SRP is presumed to be linear molecule containing no phospholipid terminal [41]. This result clearly shows that the particle size of rubber latex is an important factor affecting the molecular weight and MWD of *Hevea* rubber.

It has been reported that the rubber obtained from FL-latex by casting on glass plate and dried quickly was almost soluble in toluene or tetrahydrofuran. The gel content, insoluble rubber fraction, was less than 10%. However, when latex was processed by conventional methods and stored at a period of time, some parts of the rubber become insoluble [33]. The amount of gel phase would increase as increasing the storage period. Factors which affect the gel content are the clonal origin, processing conditions, temperature, time of drying, humidity and temperature during storage.

The gel content in commercial grade NR is variable from 5% to as high as 50%. Here, the increase in the gel content is mainly due to storage hardening caused by chemical reactions in latex, which will be discussed afterward. The MWD of commercial NR is bimodal or unimodal or unimodal with shoulder. The change from bimodal to unimodal may conceren with the shift of the peak top of low molecular-weight to the high molecular-weight one and is believed to be participated to the storage hardening and gel formation [39]. The different grades of NR produced by different processing mehtods result in the difference in molecular weights and MWD as shown in **Figure** 2.8.

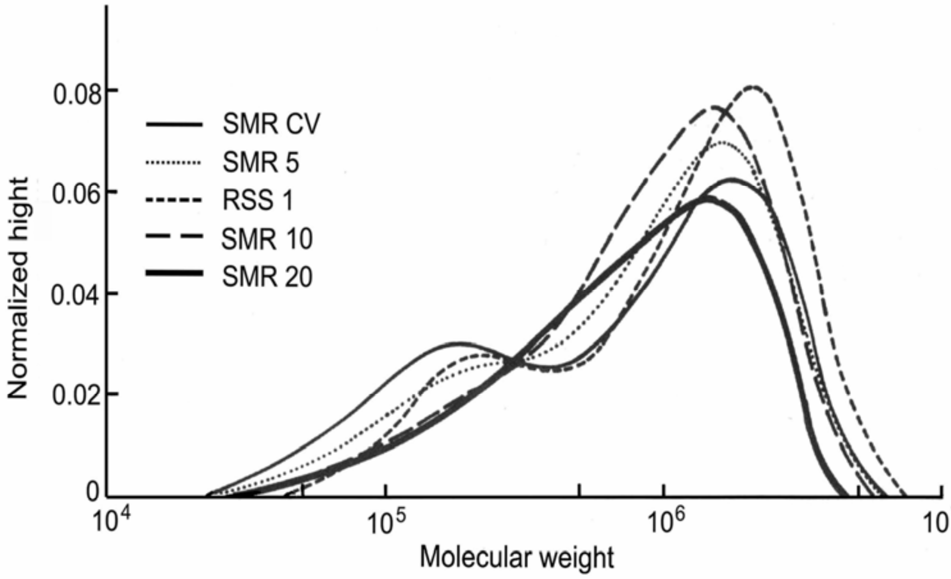


Figure 2.8 Molecular-weight distribution curves for commercial grades of NR [43].

The molecular weight of NR can be broken down under mastication, sunlight exposion and heating. The distribution become narrower and the molecular weight decreased after mastication [42]. The mechanical breakdown of rubber during premastication and compounding results in the change of MWD from bimodal to unimodal distribution. When rubber is exposed to sunlight, the surface becomes tacky due to oxidation, hence the molecular weight decreases and the bimodal distribution changes to a distribution with a broad plateau [39].

2.1.5 Purification of natural rubber

Dry natural rubber contains 6% non-rubber constituents, i.e., proteins, lipids, sugars, inorganic compounds, *etc*. Some of these non-rubber constituents have been considered to bring about prominent properties characteristic of natural rubber. A suggestion was made that the extractable proteins, which might caused Type I allergy, should be removed from rubber products made from latex; hence, washing of latex by centrifugation, enzymatic deproteinization using alkaline protease or papain, and treatment with NaOH or KOH are popular techniques to remove proteins. Deproteinized latex is now applied to the production of condoms, gloves and foam rubber to reduce the extractable protein content [43].

It is remarkable that the deproteinized natural rubber shows very low creep and stress relaxation, low compression set, good damping modulus, comparing with the conventional natural rubber [44]. This clearly indicates that proteins are not essential constituents to induce outstanding propeeties of natural rubber. On the other hand, treatment of natural rubber with sodium methoxide was found to decrease dramatically the strength of the raw rubber (referred to as green strength), to the same level as that of synthetic *cis*-1,4-polyisoprene. This suggests that the fatty acid seter and phosphoric ester groups linked to the natura; rubber molecule are essential constituents in bringing about the characteristic properties of natural rubber [45].

2.2 Hydrogenation of Unsaturated Polymers

Hydrogenation reaction of unsaturated polymers has been studied extensively. Some examples are described below.

2.2.1 Homopolymers

The structures and properties of hydrogenated polymers depend upon the precursor polymers and the extent of hydrogenation. Polymer crystallinity tends to increase with increasing hydrogenation, but glass transition temperature, depending upon the starting material.

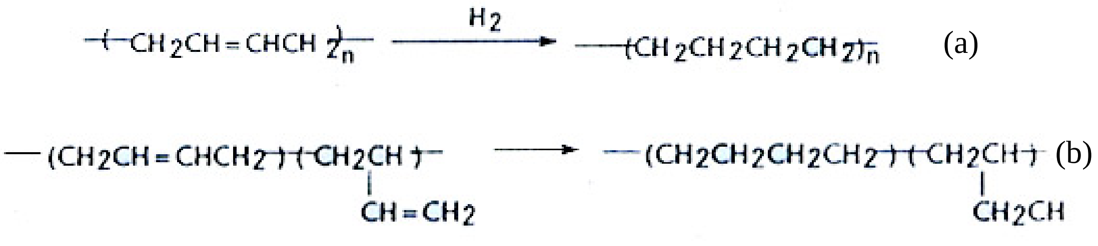


Figure 2.9 (a) Hydrogenation of 1,4 polybutadiene resulting in crystallizable polyethylene.

(b) Hydrogenation of modurate amount of 1,2 units (1,2-PB) resulting in poly (ethylene-co-butylene).

2.2.2 Copolymers

Hydrogenation of copolymers, especially block copolymers, is used to modify molecular structure of copolymers. The hydrogenated copolymers are either hydrogenated diene-diene copolymers or hydrogenated diene-aromatic copolymers. Some diblock copolymers can not be produced by other methods such as ethylene-propylene block copolymer. It starts from polybutadiene-polyisoprene block copolymer by conventional means followed by hydrogenation to produce the desire molecular structure.

2.2.3 Functional Polymers

Hydrogenation of functional polymers has also been studied. The following is the hydrogenation of poly(butadiene-co-*N*-vinylpyridine) and boron trifluoride is used as a protecting group for amine functionalities.

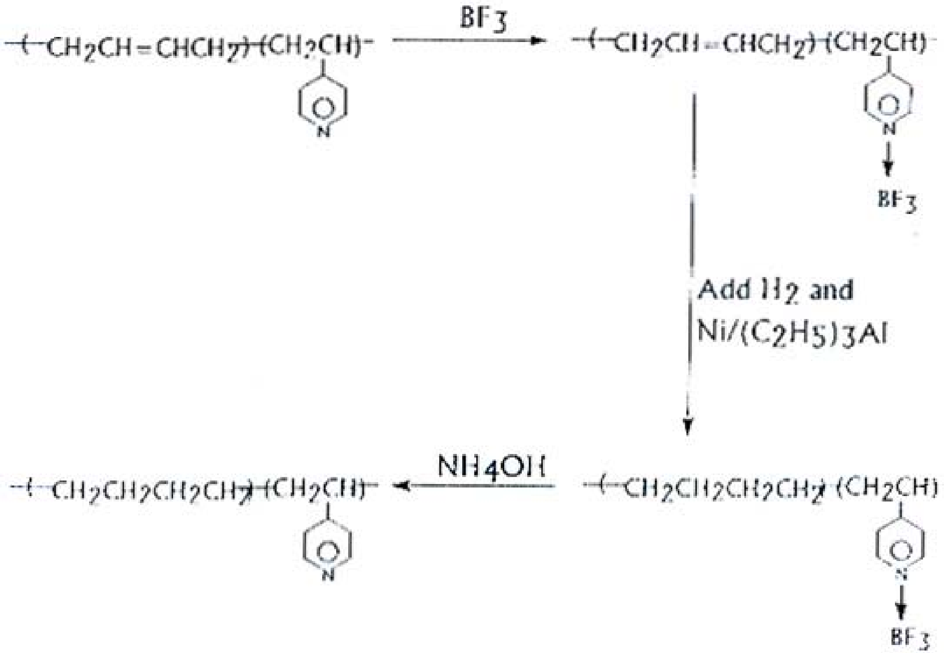


Figure 2.10 poly(butadiene-co-N-vinylpyridine) used boron trifluoride as a protecting group for amine functionalities.

2.3 Classification of different methods of hydrogeantion

Diene elastomers can be hydrogenated by catalytic method or non-catalytic method

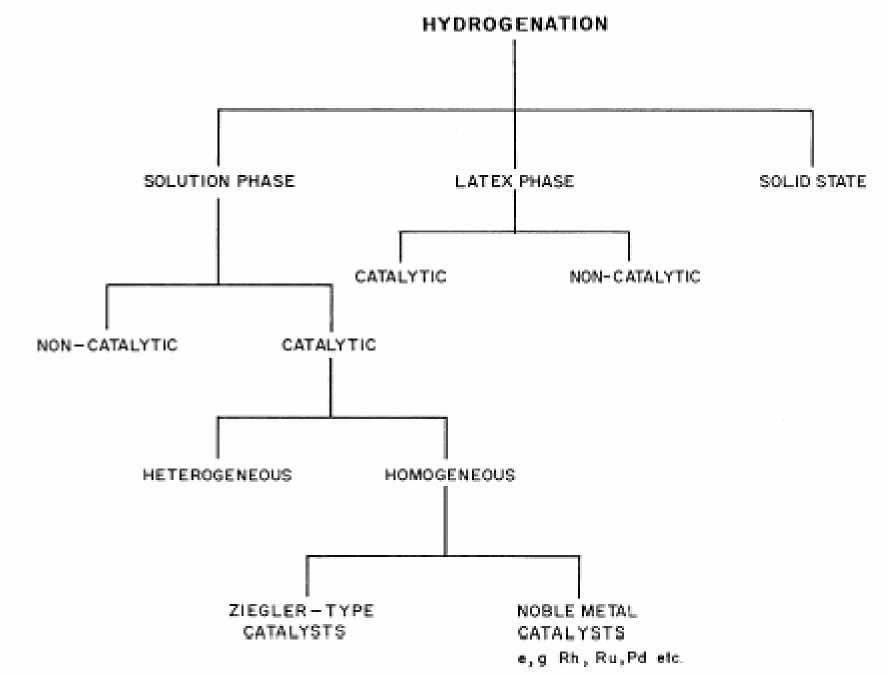


Figure 2.11 Classification of different methods of hydrogenation.

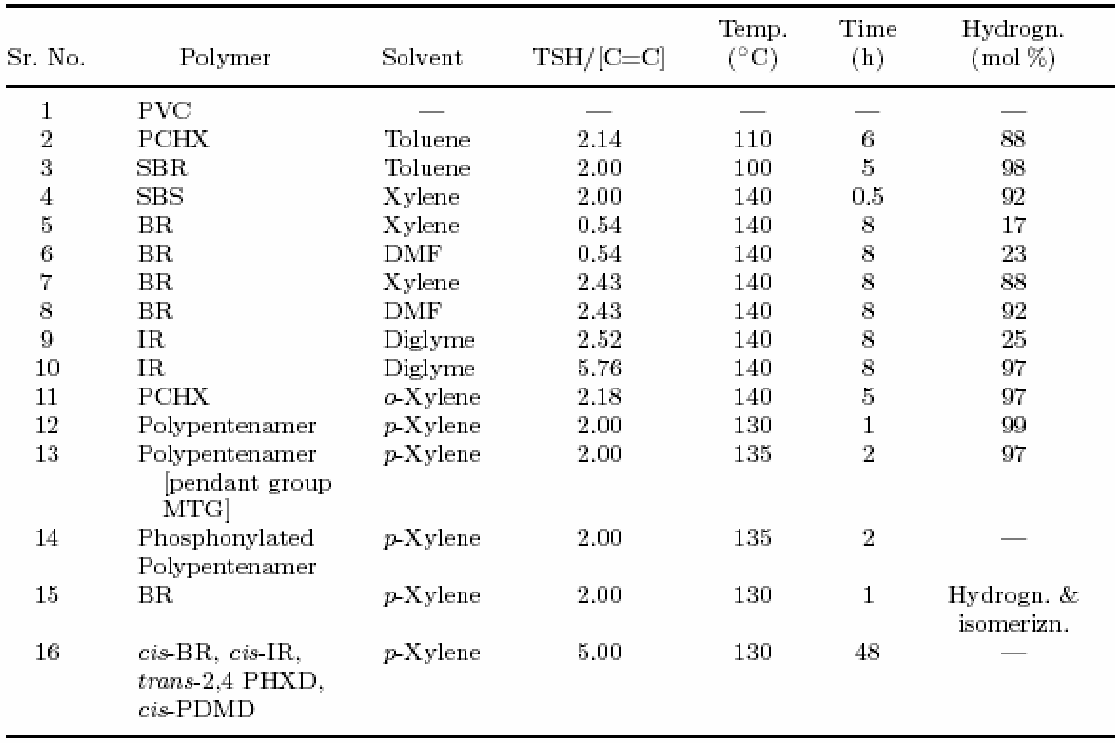
2.4 Non-catalytic Hydrogenation of diene elastomers [46]

Non-catalytic hydrogenation of unsaturated polymers is generally carried out using diimide, generated *in situ.* Hydrogenation of different elastomers using diimides is shown in Table I. Nakagawa and Okawara [47] first employed *p*-toluenesulfonyl hydrazide (TSH) as the precursor for diimide for the hydrogenation of residual unsaturation in poly(vinyl chloride). Mango and Lenz [48] studied the homogeneous hydrogenation of homopolymers of butadiene, cyclohexadiene, isoprene, and styrene-butadiene (block and random copolymers) using TSH/olefin ratio of 2.0 at elevated temperature. Harwood *et al.* [49] hydrogenated 1,4-BR and 1,4-IR with different TSH/olefin ratio. Quantitative hydrogenation can be achieved at TSH/olefin ratio of about five. The relative rates of hydrogenation decrease in the order, vinyl > cis ≥ trans.

Sanui *et al.* [50] hydrogenated polypentenamer in *p*-xylene with TSH. Analysis of the hydrogenated polypentenamer showed absence of degradation or side reactions. They also hydrogenated polypentenamer having different pendant groups (like methyl thioglycolate [51] and phosphoric acid [52]) using TSH. The pendant groups were not affected. Chen [53] showed that the reaction of TSH and BR not only hydrogenates the carbon-carbon double bonds but also isomerizes the remaining double bonds in the polymer. Nang *et al.* [54] hydrogenated IR with TSH and studied its physical and mechanical properties. Hydrogenated IR (HIR) was found to possess inferior tensile properties compared to the parent polymer. Hseih and Yeh [55] reported the hydrogenation of BR, IR, *cis*-1,4-poly(2,3-dimethylbutadiene) (*cis*-PDMB), and *trans*-1,4-poly(2,3-hexadiene)(*trans*-2,4-PHXD), using a five-fold excess of TSH for a period of 24 h. The microstructures of the parent polydienes and the degree of hydrogenation of hydrogenated products were determined by IR and ^{1}H-NMR and ^{13}C-NMR. The relative activity in the hydrogenation of 1,4 polydienes with diimide showed the following order BR > IR > *trans*-2,4-PHXD > *cis*-PDMD > *trans*-PDMB.

Hydrogenation using diimde is generally carried out at elevated temperatures (110 to 160°C) and in high boiling aromatic solvents. At high temperature *p*-toluenesulfonyl hydrazide (TSH) undergoes decomposition to form reactive diimide (N_2H_2) which subsequently reduces carbon-carbon double bonds. The addition of diimide to double bond occurs in a cis fashion [56]. The diimide hydrogenation is stoichiometric and hence, unsuitable for large scale processes. It promotes *cis-trans* isomerization of 1,4-dienes. Another possible side reaction is the attachment of hydrazide fragments into the polymer. Since the reaction is carried out at high temperature, it causes degradation and cyclization of polymers leading to inferior physical and mechanical properties.

Table 2.3 Non-catalytic hydrogenation of diene elastomer using *p*-toluenesulfonyl hydrazide (TSH)



Sr. No.	Polymer	Solvent	TSH/[C=C]	Temp. (°C)	Time (h)	Hydrogn. (mol %)
1	PVC	—	—	—	—	—
2	PCHX	Toluene	2.14	110	6	88
3	SBR	Toluene	2.00	100	5	98
4	SBS	Xylene	2.00	140	0.5	92
5	BR	Xylene	0.54	140	8	17
6	BR	DMF	0.54	140	8	23
7	BR	Xylene	2.43	140	8	88
8	BR	DMF	2.43	140	8	92
9	IR	Diglyme	2.52	140	8	25
10	IR	Diglyme	5.76	140	8	97
11	PCHX	*o*-Xylene	2.18	140	5	97
12	Polypentenamer	*p*-Xylene	2.00	130	1	99
13	Polypentenamer [pendant group MTG]	*p*-Xylene	2.00	135	2	97
14	Phosphonylated Polypentenamer	*p*-Xylene	2.00	135	2	—
15	BR	*p*-Xylene	2.00	130	1	Hydrogn. & isomerizn.
16	*cis*-BR, *cis*-IR, *trans*-2,4 PHXD, *cis*-PDMD	*p*-Xylene	5.00	130	48	—

Catalytic hydrogenations are of two types depending on the state of the catalyst and the substrate in the reaction medium.

2.5 Heterogeneous catalytic hydrogenation [46]

In heterogeneous hydrogenation the catalytically active species and the substrate are in two different phases. Usually this kind of hydrogenation is carried out by stirring a solution of polymer to be reduced with an insoluble catalyst under hydrogen atmosphere. The hydrogenated polymer is isolated simply by filtration of the catalyst, followed by evaporation of the solvent. The selection of solvent, reaction temperature, and hydrogen pressure depends on the nature of the polymer and the catalyst chosen. The efficiency of the heterogeneous catalyst depends on its surface area and the nature of support. Catalyst with lower activity such as NiO requires high temperature and pressure, and thus leads to degraded products having inferior properties. But more active catalysts like platinum, rhodium, ruthenium, and palladium need milder conditions and give products with higher structural integrity.

Staudinger [57] first used platinum metal as a heterogeneous catalyst for the hydrogenation of natural rubber to elucidate its structure. Jones [58] hydrogenated BR and IR with nickel on kieselguhr using cyclohexane as the solvent. He achieved 70% hydrogenation of the elastomer. Yakubchik and Gromova [59] hydrogenated IR in hexane solution at room temperature and pressure using Pd/$CaCO_3$, Pd/Ni and Pt/C (activated with chloroplatinic acid) as catalysts. The activity of the catalysts gradually declined and the viscosity of the solution progressively decreased with increasing degree of hydrogenation.

Gregg [60] hydrogenated IR (*cis* and *trans*), poly-2-ethylbutadiene, poly-2-*n*-propylbutadiene and poly-2-phenylbutadiene using Raney nickel as catalyst. In this case, catalyst to polymer ratio, time and temperature had a major effect on the degree of hydrogenation. Complete hydrogenation was achieved at 240°C and 2.4 MPa H_2 pressure at 48 h.

Functional as well as endcapped polymers can also be hydrogenated using heterogeneous catalysts. Karaivanova *et al.* [61] carried out the reduction of nitrated oligomeric natural rubber and BR with hydrogen in a weak acid medium using Raney-nickel catalyst. Hydroxy terminated IR was hydrogenated using nickel-diatomaceous earth [62], nickel-kieselguhr [63] or reduced nickel catalysts [64]. Rosedale and Bates [65] performed the complete hydrogenation of 1,2-BR [99% 1,2 i,e poly(vinylethylene)] using palladium on $CaCO_3$. This catalytic hydrogenation proceeds by concerted hydrogenation of approximately 85% of the unsaturated units of poly(vinylethylene), during a single adsorption step. They explained it by using the adsorption energy of saturated and unsaturated simple hydrocarbon molecules on group VIIIA metals. Bates *et al.* [66] hydrogenated *cis*-1,4-polyisoperene-1,2-BR diblock copolymer using Pd on $CaCO_3$ to produce a model poly(ethylene-propylene){poly(ethyl-ethylene) diblock copolymer.

Takenaka *et al.* [67] hydrogenated poly(2-silyl substituted 1,3-butadiene) by varying substitution on silicon. Saturation of carbon-carbon double bonds was obtained regardless of the substitution on silicon atom. Supported nickel [68] and palladium catalysts [69-71] have been used to hydrogenate copolymers having tetracyclic ring. Styrene-butadiene random copolymers and styrene-butadiene block copolymers are very useful elastomers and thermoplastic elastomers. Because of the presence of carbon-carbon unsaturation it has poor resistance to oxidative and ozonolytic degradation. This can be avoided by hydrogenation of these elastomers. Fukawa *et al.* [72] used rhodium on carbon or alumina catalysts for the selective hydrogenation of butadiene-styrene and isoprene-styrene copolymers. The resultant copolymers showed good resistance to heat and weathering. A solution of 70:30 styrene-butadiene block copolymers (70:30) in 900 g cyclohexane was hydrogenated with 20 g 5% rhodium on carbon under 49.05 MPa hydrogen pressure at 80°C for 90 minutes. The catalyst was recovered from the solution simply by filtration and could be reused. The extent of hydrogenation was 89% and 12% hydrogenation for butadiene and styrene portions respectively. SBR was also hydrogenated using nickel catalyst [73], $PdCl_2$ and $RhCl_3$ [74] (supported on carbon). Beova *et al.* [75] studied the reduction of polyfunctional nitro oligomers from styrene-butadiene rubber using Raney-nickel catalyst.

Diene polymers have been hydrogenated using colloidal noble metals prepared by heating the noble metal compound in alcohol in presence of polar polymers [76]. $RhCl_3$, $3H_2O$ (0.5 g), and poly(vinyl pyrrolidinone) in ethanol were refluxed for 30 minutes to obtain a 0.25 g/L dispersion of colloidal rhodium. A solution of 10 g styrene-butadiene block copolymer in 200 L THF and 40 mL of the above dispersion were reacted under 0.5 MPa hydrogen pressure at 180°C for 40 minutes to give a product of 71% and 0% hydrogenation based on butadiene and styrene units, respectively. They also prepared the colloidal noble metal dispersion by a different method. [77] In this method a mixture of $RhCl_3{\cdot}3H_2O$ (0.5 g), 8.56 g poly(vinyl pyrrolidinone), and 0.4 g NaOH in methanol was refluxed to give a 0.25

g/L colloidal rhodium dispersion. With this catalyst 72% hydrogenation was achieved in only 20 min under 0.5 MPa hydrogen pressure and at 18°C. Huckul [78] developed a heterogeneous catalyst containing group VII metals on porous support of pore size more than 45 nm. Diatomaceous earth was impregnated with aqueous solution of palladium chloride and dried to give a catalyst containing 5% palladium. Hydrogenation of styrene-isoprene rubber in cyclohexane over this catalyst at 90°C for 20 h gave 92% hydrogenation, whereas 5% hydrogenation was achieved with palladium on alumina as the catalyst. Polystyrene has also been hydrogenated using the supported metal catalysts. In this case more drastic reaction conditions are required to reduce the aromatic nucleus. Ishihara and Kuramoto [79] hydrogenated syndiotactic polystyrene using ruthenium on carbon under 10 MPa hydrogen pressure, at 150°C for 4 h to give heat resistant syndiotactic poly(vinyl cyclohexane). Atactic polystyrene has also been hydrogenated using palladium on SiO_2 [80] and palladium on carbon [81].

Hydrogenated nitrile rubber (HNBR) is a useful high performance elastomer having excellent resistance to oxidative, ozonolytic and thermal degradation and to fluids at high temperature. Nippon Zeon Co. Ltd., Japan commercialized HNBR under the trade name Zetpol®. From an examination of patent literature it is apparent that 5% palladium on carbon was one of the earlier catalyst system employed. Only 47% hydrogenation was obtained using this catalyst. By modifying the reaction conditions and particle size of the carbon, the extent of hydrogenation was improved. Further improvement in the catalytic activity was demonstrated by impregnating calcium into the heterogeneous catalyst system. A solution of NBR in acetone was selectively hydrogenated using Pd-Ca supported on carbon at 50°C and under 5.0 MPa hydrogen pressure. Hydrogenation to the extent of 95% was achieved without the reduction of nitrile group. When a solution of NBR in acetone was hydrogenated using palladium-aluminum on carbon under 5.0 MPa hydrogen pressure and at 50°C, 92% hydrogenation was achieved within 4 h.

During hydrogenation of diene polymers using supported catalyst, it is observed that the use of carbon black with surface area greater than 800 m^2/g (and dibutylphthalate adsorption higher than 2.50 mL/g) remarkably improves hydrogenation efficiency.22 $PdCl_2$ and $RhCl_3$ were supported on Ketjenblack E.C.

(having dibutylphthalate adsorption 3.40 mL/g and surface area 1000 m^2/g) and used for the hydrogenation of NBR, SBR, BR and IR. Palladium supported on silica [82, 83] has also been used to hydrogenate NBR. The activity of this catalyst increases when lithium acetate (LiOAc) is used as a promoter. [84] Watanabe and Kubo [85] hydrogenated NBR in isobutylmethyl ketone over palladium on carbon catalyst and washed with NaOH to give a rubber with iodine value 31. Sawanbory and Furuki [86] prepared heat resistant and oil resistant HNBR in the presence of palladium on carbon under hydrogen pressure. Buding and Rudolf [87] hydrogenated NBR in acetone with palladium supported on alkaline earth carbonate which have high mechanical strength and can be readily recovered and reused. A solution of NBR (37.4 g) in acetone (337 g) with 3.75 g Pd (5%) on $CaCO_3$ was hydrogenated under 50 MPa hydrogen pressure at 50°C for 4 h to get 98.5% hydrogenation.

2.6 Homogeneous catalytic hydrogenation [46]

In homogeneous catalysis the catalytically active species is molecularly dispersed in the polymer. The main principle of homogeneous hydrogenation reaction is the activation of molecular hydrogenation by transition metal complexes in solution and the subsequent transfer of hydrogen to the unsaturated substrate. An important characteristic of the homogeneous system is their high selectivity when compared to heterogeneous systems. The homogeneous catalysis also provides opportunity for enhancing the reactivity and selectivity of the metal centered catalysts through the suitable modification of the ligand system. For example, $Ru(X)(CO)L_2$ [where X = H or β-styryl, L is a bulky phosphine such as tricyclohexyl] is a better catalyst than $RuCl_2(PPh_3)_3$ for the hydrogenation nitrile-butadiene copolymers. Homogeneous catalysis also facilitates the study of mechanisms involved in the catalytic cycle. Homogeneous catalytic hydrogenation can be classified into two types.

2.6.1. Homogeneous hydrogenation using Nobel Metal catalysts

Homogeneous hydrogenation using noble metal catalysts is a prevalent method in organic chemistry [87]. The main features of these catalysts are that they can tolerate olefins having diverse functional groups and show interesting selectivity patterns. Hydrogenation of functional diene homopolymers or copolymers presents special problems because many of the functional groups are not compatible with the catalysts. These problems are particularly acute for highly coordinating functionalities such as nitrile, carboxyl, amino, hydroxyl, etc. Moreover when the polymer contains two or more functional groups which are all prone to reduction, careful selection of the catalyst system and reaction condition becomes important if regiospecificity during hydrogenation is desired. The major breakthrough in the history of selective homogeneous hydrogenation is the discovery of Wilkinson's catalyst *i.e. tris*-triphenylphosphinechloro rhodium(I) [88]. This homogeneous hydrogenation catalyst offers remarkable activity as well as selectivity towards carbon-carbon double bond in presence of other reducible functional groups.

2.6.1.1 Rh based catalysts

Acrylonitrile{butadiene copolymers (NBR) are elastomers which are extensively used in fluid and oil-field application because of its excellent oil resistant properties. Hydrogenated nitrile rubber (HNBR) is an excellent example of chemical modification of elastomers for improving performance. Recent literature reveals that homogeneous catalysts based on noble metals are increasingly being used for the preparation of HNBR. Although they are more expensive when compared to nickel and cobalt complexes, their high selectivity, hydrogenation efficiency and properties of the resulting saturated polymers partially offsets the cost factor.

The first example of hydrogenation of NBR is due to Bayer A.G. [89] using $RhCl(PPh_3)_3$ catalyst in chlorobenzene as solvent, a polymer with complete saturation of vinyl and trans double bonds could be obtained. Weinstein [90] prepared elastomeric tetramethylene-ethyl-ethylene-acrylonitrile copolymers by selective hydrogenation of NBR in presence of $RhCl(PPh_3)_3$ and excess triphenyl phosphine. Almost complete hydrogenation was obtained at both low and high hydrogenation pressure. The reaction temperature and pressure necessary for hydrogenation depends on the catalyst concentration. Rempel *et al.* [91] conducted a detailed study of the hydrogenation of NBR in presence of $RhCl(PPh_3)_3$. The reaction was carried out in methylethyl ketone (MEK) at 40°C under a hydrogen pressure < 101.32 KPa. The selectivity of the catalyst for terminal vs. internal double bonds in the polymer was markedly influenced by the nature of the solvent. In MEK the catalyst did not exhibit selectivity for the hydrogenation of 1,2 over 1,4 units of the copolymer, whereas distinct preference towards saturation of 1,2 units was observed when the reaction medium was chlorobenzene. The hydrogenation showed a first order dependence of rate on concentration of catalyst and hydrogen $[H_2]$ (when $[H_2] < 1.0$ mM). At higher pressure, the rate of hydrogenation was zero order with respect to hydrogen concentration (when $[H_2] > 1.0$ mM). A mechanism consistent with the kinetics and the experimental observation was proposed (**Figure 2.12**).

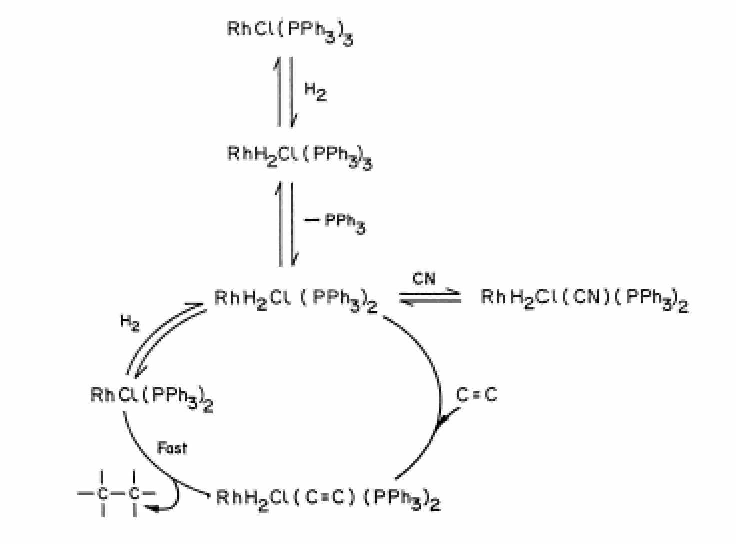


Figure 2.12 Mechanism of hydrogenation of NBR using $RhCl(PPh_3)_3$.

Bhattacherjee *et al.* [92] examined in detail the conditions for hydrogenation of NBR using $RhCl(PPh_3)_3$ in chlorobenzene solvent. They observed that there was no hydrogenation at room temperature. However, the extent of hydrogenation increased with the increase in temperature, hydrogen pressure, and catalyst concentration. They found that quantitative hydrogenation of NBR can be obtained at a catalyst concentration of 0.02 mmol under 5.6 MPa hydrogen pressure at 100°C for 11 h. The amount of catalyst required for complete hydrogenation in chlorobenzene solution is much lower than that in MEK solution. No degradation or side reaction occurred during the hydrogenation of NBR and molecular weight of the elastomers did not change significantly.

BR has been hydrogenated using Rh, Ru, and Pd based catalysts. Hydrogenation of 1,4-BR leads to crystalline polyethylene whereas hydrogenation of BR containing moderate amount of 1,2 units gives products which show elastomeric behavior.

Kang [93] hydrogenated BR using $RhHCO(PPh_3)_3$ as well as $RuHCl(PPh_3)_3$ at 25-45°C under 0.2 to 1.0 MPa hydrogen pressure. Polymeric catalysts [94] containing organorhodium and organophosphorus pendant groups are also used to hydrogenate BR. High vinyl content (88%) butadiene rubber was hydrogenated using polystyrene beads having pendant $PPh_2Rh(PPh_3)_2Cl$ at 110°C under 2.3 MPa hydrogen pressure in 3 h to give 93%hydrogenation. Doi *et al.* [95] carried out the hydrogenation of 1,4, atactic 1,2 and syndiotactic 1,2-BR in toluene using $RhCl(PPh_3)_3$ at 100°C under 5.0 MPa hydrogen pressure. They obtained complete hydrogenation in 24 h. Hydrogenation proceeded without any chain scission. Rempel *et al.* [96,97] studied the detailed kinetics and mechanism of the hydrogenation of BR in presence of $RhCl(PPh_3)_3$. They observed that complete hydrogenation of 1,2-BR can be achieved easily whereas complete hydrogenation of 1,4-BR could not be obtained due to the precipitation of the partially saturated polymer under the reaction conditions employed. The detailed investigation of the hydrogenation of 1,4-BR using $RhCl(PPh_3)_3$ in *o*-dichlorobenzene was carried out at 65°C in order to gain insight into the mechanism of the reaction. The reaction exhibits apparent first-order dependence on the concentration of C=C. The hydrogenation rate is first order with respect to the concentration of catalyst and the concentration of hydrogen at low hydrogen concentration and zero order at higher hydrogen concentration. Under this reaction conditions, the $RhCl(PPh_3)_3$, catalyst showed selectivity for the hydrogenation of 1,2 (vinyl) units over 1,4 (internal) units present in the BR. It is reported that in the absence of added triphenylphosphine, the catalyst forms dimers which would complicate the reaction mechanism [98].

$$2RhCl(PPh_3)_3 \longrightarrow [Rh(\mu - Cl)(PPh_3)_2]_2 + 2PPh_3$$

So, in all cases excess triphenylphosphine is added to retard the dimer formation. The rate of hydrogenation is inversely proportional to the concentration of triphenylphosphine. The kinetic study indicates that the hydrogenation occurs by the hydride path (**Figure 2.13**). The catalyst $RhCl(PPh_3)_3$ reacts with hydrogen to form dihydride complex [99], $RhH_2Cl(PPh_3)_3$ which rapidly transfers two hydrogen atoms to the carbon-carbon double bonds to form saturated polymers.

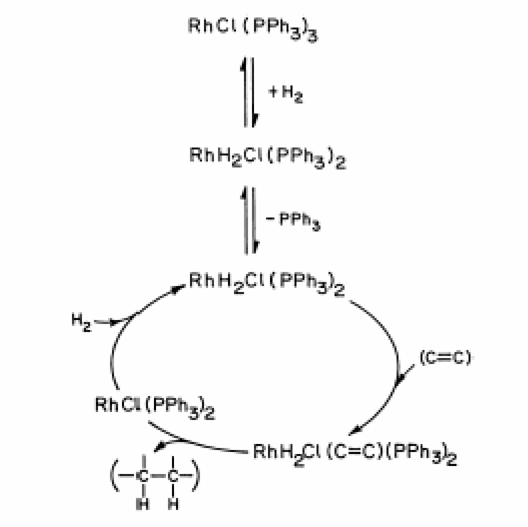


Figure 2.13 Catalytic cycle of hydrogenation of polybutadiene (BR) using $RhCl(PPh_3)_3$.

Mohammadi and Rempel [100] hydroformylated BR (90% 1,2 unit) using $RhH(CO)(PPh_3)_3$ in toluene. The hydroformylated BR was subsequently hydrogenated directly using $RhClH(CO)(PPh_3)_3$ as catalyst to get polyethylene having -OH and $-CH_2OH$ (hydroxymethyl) groups as the pendant groups. Recently Jin *et al.* [101] carried out the hydrosilylation of BR (with different 1,2 content) with trialkyl silane followed by the complete hydrogenation. Sibatain and Rempel [102] carried out hydroformylation of styrene-butadiene copolymers using $RhH(CO)(PPh_3)_3$. The hydroformylated copolymers were hydrogenated with $RuH(CO)(PPh_3)_3$ to achieve hydroxymethylated polymers.

Bouchal *et al.* [103] hydrogenated hydroxyl terminated telechelic BR using $RhCl(PPh_3)_3$ in toluene. They prepared two types of prepolymers by anionic and radical polymerization. They studied the detailed kinetics of this hydrogenation reaction. Due to the predominant 1,2 structural units the anionic prepolymer reacted twice as fast as the radical prepolymers with hydrogen ($k = 0.093\ mol^{-1}\ dm^3\ s^{-1}$). There is a partial loss of hydroxyl groups in the modified telechelic prepolymers. The extent of the loss of hydroxyl groups can be controlled by regulating the concentration of the hydrogenation catalyst, the partial pressure of hydrogen, temperature and reaction time.

Recently Kato *et al.* [104] have reported new Rh complexes for the hydrogenation of hydroxyl terminated telechelic butadiene rubber without any loss of -OH group from the polymer. They selectively hydrogenated hydroxyl terminated liquid BR using dihydrido (1,3-diphenyl ariazenido) [bis(1,2-diphenyl phosphino benzene)]rhodium(III) complex as the catalyst. With this catalyst no loss of hydroxyl was observed.

The random and block copolymers of styrene and butadiene can be hydrogenated using Rh and Ru based catalysts. There are very few examples of hydrogenation of these copolymers using noble metal catalysts. Kato *et al.* [105] used a new rhodium complex (**Figure 2.14**) to hydrogenate styrene-butadiene copolymer in toluene.

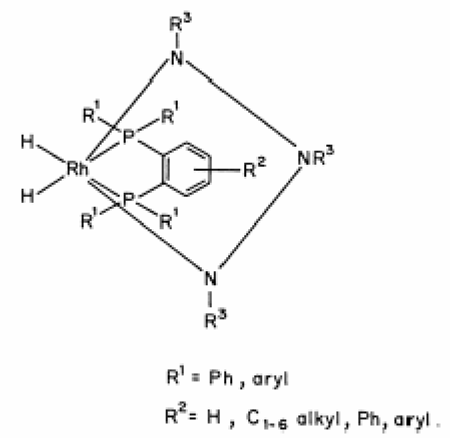


Figure 2.14 Structure of new Rh complex used for the hydrogenation of OH-terminated BR and SBR.

Guo *et al.* [106] used $RhCl(PPh_3)_3$ for the hydrogenation of styrene-butadiene block copolymer in toluene as well as in *p*-dichlorobenzene. They studied the detailed kinetics and mechanism for this hydrogenation reaction. The kinetics resembles that of BR hydrogenation. But the apparent entropy of activation of SBS (-88.5 J mol^{-1} K^{-1}) is much higher than that of 1,2-BR (-10.5 J mol^{-1} K^{-1}) and 1,4-BR (-26.0 J mol^{-1} K^{-1}). This can be explained by steric effects caused by the pendant aromatic rings present in SBS copolymer. The mechanism of hydrogenation of this copolymer is same as shown for the hydrogenation of BR (**Figure 2.13**).

Singha *et al.* [107] also studied the hydrogenation of chloroprene elastomers (CR) in presence of $RhCl(PPh_3)_3$. It was expected that hydrogenation of CR would lead to a hitherto unknown ethylene-vinyl chloride alternating copolymer. It was observed that the catalytic hydrogenation of CR yields a product with predominantly linear polyethylene sequence with minor proportion of *alt* (ethylene-*co*-vinyl chloride) copolymer. This was attributed to the dehydrochlorination of CR. The relative components of different structural units can be obtained by regulating the catalyst concentration, temperature, hydrogen pressure and the reaction time. It was proposed that similar to other diene polymers $RhCl(PPh_3)_3$ reacts with hydrogen to form dihydrdo complex which coordinates with CR at the carbon α to the -Cl group. This undergoes dehydrochlorination to form carbon-carbon double bonds which are subsequently converted to polyethylene by hydrogenation in presence of $RhCl(PPh_3)_3$ (**Figure 2.15**).

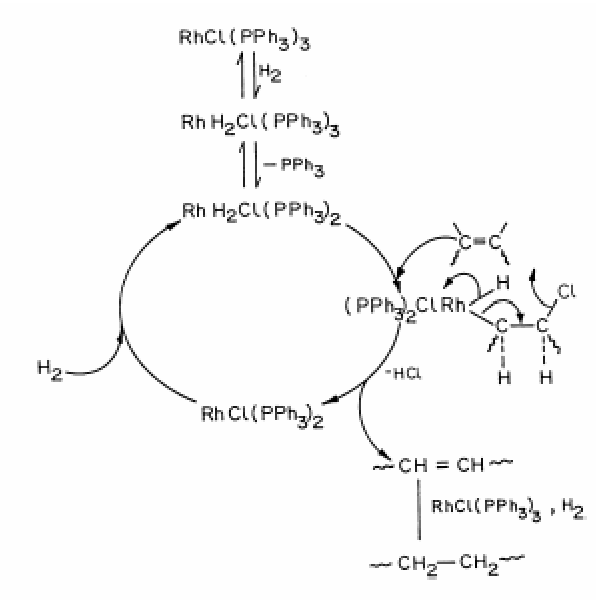


Figure 2.15 Catalytic cycle of hydrogenation of chloroprene rubber (CR) using $RhCl(PPh_3)_3$.

2.6.1.2 Ru based catalysts

The hydrogenation of NBR using homogeneous ruthenium catalysts has been reported by Buding *et al.* [108] In this case NBR is dissolved in MEK, mixed with chlorobenzene solution of $RuCl_2(PPh_3)_3$ and reacted under hydrogen pressure to give a product with 99% hydrogenation. Chlorinated solvent and low molecular weight ketone are used as the reaction medium. Ruthenium is cheaper than the rhodium and hence offers economical advantages. However, hydrogenation using ruthenium based catalysts require high temperature and high pressure which lead to degradation and gel formation in the polymers [109]. Ruthenium forms inactive Ru-CN species by coordination with -CN group of NBR. It also induces the isomerization of C=C.

In view of this, the rate of hydrogenation of NBR using ruthenium based catalysts is very poor and it is very difficult to get quantitative hydrogenation. To improve the reaction rate many organic or inorganic additives (like Et_4NCl, [110] $CaCl_2$ [111] and CH_3COOH [112]) have been suggested in the literature. Efficiency of hydrogenation can also be improved by changing or by modifying the ligands around the Ru center.

Rempel and Guo [109] studied the hydrogenation of NBR using RuCl(CO)(OCOR) under different hydrogen pressures. At 28.6 MPa hydrogen pressure quantitative hydrogenation was achieved in 3 h and the cyano group remained unaffected. When the reaction was carried out at 19.0 MPa hydrogen pressure, 98.5% hydrogenation was achieved in a period of more than 10 h. However, at atmospheric pressure only 40% hydrogenation was achieved. Ruthenium complexes cause a shift of unsaturation to a position α to the -CN group (which is also in conjugation with the -CN group). Thus, isomerization is one of the reasons for incomplete hydrogenation. The detailed kinetics of hydrogenation of NBR was investigated to understand the reaction mechanism.

The rate of hydrogenation was first order with respect to [C=C] and ($[H_2]$). It also shows a first order dependence of [Ru] at low Ru concentration. At higher catalyst concentration, the hydrogenation rate becomes insensitive to further increases in the [Ru]. It may be due to the formation of dimer of Ru complex at high ruthenium concentration. The rate of hydrogenation decreases with the increase of nitrile content in the polymer. This implies that -CN group co-ordinates with the Ru center of the complex. The rate of hydrogenation also decreases with increase in the concentration of triphenylphosphine. Based on kinetic results Rempel suggested a mechanism of hydrogenation of NBR (**Figure 2.16**).

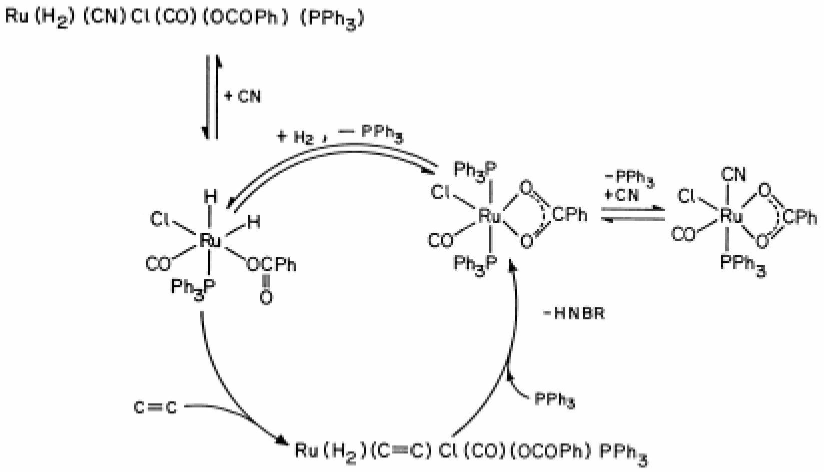


Figure 2.16 Mechanism of hydrogenation of NBR with Ru based homogeneous catalysts.

Rempel *et al.* [113] prepared a number of Ru complexes for the hydrogenation of NBR. They found that the catalysts having the best catalytic activity were of the form $Ru(X)Cl(CO)(L)_2$ (where *x* = H or β-styryl, and L is a bulky phosphine such as tricyclohexyl and triisopropyl phosphine). All these catalysts lead to quantitative hydrogenation of NBR at 130°C under 3.9 MPa hydrogen pressure. PC_4H_3 (tricyclohexyl phosphine) is more basic than PPh_3. Thus the Ru center coordinated with PC_4H_3 is more electron rich and therefore has less affinity for the electronegative nitrile group. Thus it results in less gel formation and quantitative hydrogenation.

More recently Rempel and Guo studied the hydrogenation of NBR using carbonyl chlorohydrido bis(tricyclohexylphosphine) ruthenium(II) in presence of inorganic additives[114]. In this case 10.0 g NBR was dissolved in 90 mL of chlorobenzene. The inorganic additives (like $FeSO_4$, $(NH_4)_2SO_4$, $CoSO_4$ etc.) dissolved in 1 mL of water and the catalyst of a concentration of 0.05 weight percent based on NBR were added to the NBR solution. The hydrogenation was carried out at 145°C under 8.0 MPa pressure. 99.8% hydrogenation was achieved in 3 h without significant change in the intrinsic viscosity.

Singha and Sivaram [115] examined ruthenium complex [$RuCl_2(PPh_3)_3$] for the hydrogenation of styrene-butadiene random copolymer (SBR). They studied the detailed kinetics of the reaction and suggested a mechanism based on the observed kinetics and known behavior of Ru complexes. The reaction is first-order with respect to the carbon-carbon double bond. The rate of hydrogenation has the first-order dependence on the Ru concentration and the inverse dependence on the added triphenylphosphine concentration as observed in the case of Rh complexes. The rate of hydrogenation increases with increasing hydrogen pressure as well as reaction temperature. The mechanism of hydrogenation of SBR using $RuCl_2(PPh_3)_3$ has been shown in **Figure 2.17**. In this case Ru based Wilkinson catalyst reacts with hydrogen to form hydrido complex $RuHCl(PPh_3)_3$ which is the reactive species in the hydrogenation cycle.

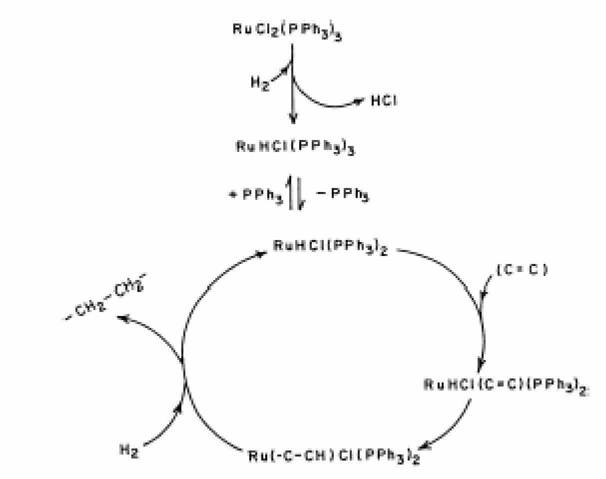


Figure 2.17 Catalytic cycle of hydrogenation of SBR using $RuCl_2(PPh_3)_3$.

2.6.1.3 Pd based catalysts

The main characteristic of the Pd based catalysts is that they require milder reaction conditions than the Ru based catalysts.

Nippon Zeon Co. Ltd. [116] patented the hydrogenation of NBR using $Pd(OAC)_2$ in acetone solution. The catalyst solution in acetone was first reduced at 20°C under hydrogen pressure of 5.0 MPa in the autoclave followed by addition of NBR solution. At 50°C and under 4.9 MPa hydrogen pressure, 97 mol%

hydrogenation was obtained in 3 h. They further improved this method by using a reducing agent like hydrazine [117]. Shell Oil Co. [118] prepared a catalyst by the combination of TEAL and Pd(2-ethylhexanoate)$_2$ [Al/Pd = 0.3]. NBR was hydrogenated with this catalyst at 60°C and 6.0 MPa hydrogen pressure in MEK to obtain 90% hydrogenation in 30 minutes. There was an increase in the rate of hydrogenation using MAO as reducing agent instead of TEAL.

Bhattacherjee *et al.* [119] studied the hydrogenation of NBR using palladium acetate [Pd(OAC)$_2$] catalyst in acetone solution. 96% hydrogenation could be obtained at 100°C under 2.7 MPa hydrogen pressure. The detailed kinetics of the NBR hydrogenation was also investigated. The rate of hydrogenation increased with increasing hydrogen pressure and catalyst concentration. The reaction was first order with respect to olefinic substrate at higher pressure. The apparent activation energy, enthalpy, and entropy of the reaction were calculated as 29.9 kJ/mol, 27.42 kJ/mol, and -0.20k/mol/K respectively. Bhattacherjee *et al.* [120] hydrogenated epoxidized natural rubber (ENR) in acetone/chloroform mixture using Pd(OAC)$_2$ as catalyst. In this case olefinic unsaturation was selectively reduced without affecting the epoxy groups. However, the reaction rate decreased as the epoxy content in ENR increases. They proposed a mechanism of this hydrogenation reaction. Palladium (II) acetate has an unusual trimeric structure consisting of three metal atoms held together by six bridging acetate groups [121]. When the catalyst is dissolved in an organic solvent having the donor atoms it dissociates to form monomeric species. In presence of hydrogen these species form hydride complexes which coordinate with carbon-carbon double bonds which in turn, on hydrogen transfer, form saturated products (**Figure 2.18**).

Bhattacherjee *et al.* [122] used a new homogeneous palladium (II) catalyst to hydrogenate NBR in $CHCl_3$. They prepared a six member cyclopalladate complex of 2-benzoylpyridine [Pd(CH_3COO)($C_6H_5COC_5H_4N$)]$_2$ (**Figure 2.19**) based on Pd metal..

Using this catalyst they hydrogenated liquid carboxylated nitrile rubber (L-XNBR). The main feature of this catalyst is that it does not lead to decarboxylation of the L-XNBR as observed in case of Pd(OAC)$_2$ and RhCl(PPh$_3$)$_3$ catalysts [123]. 8 80% hydrogenation was achieved in $CHCl_3$ solvent under 5.6 MPa hydrogen pressure at 75°C in 6 h. The reaction kinetics exhibits apparent first-order dependence with respect to the olefinic substrate. An increase in the amount of nitrile and carboxyl decreases the rate constants of the reaction. The activation energy of L-XNBR hydrogenation is 20.20 kJ/mol. Takahashi and Kubo [124] hydrogenated NBR in acetone solution using $(MeCN)_2PdCl_2$ at 50°C under 5.0 MPa hydrogen pressure. They obtained 85% hydrogenation in 6 h whereas only 5% with $PdCl_2$ catalyst. Patterson [125] prepared a new catalyst of palladium by treating $PdCl_2$ with aqueous NaOH solution to form a precipitate which was washed to form a hydrated palladium oxide. It was extracted using acetonitrile as solvent. 70% hydrogenation of NBR was achieved with this homogeneous catalyst at 75-85°C and 2.41 MPa hydrogen pressure.

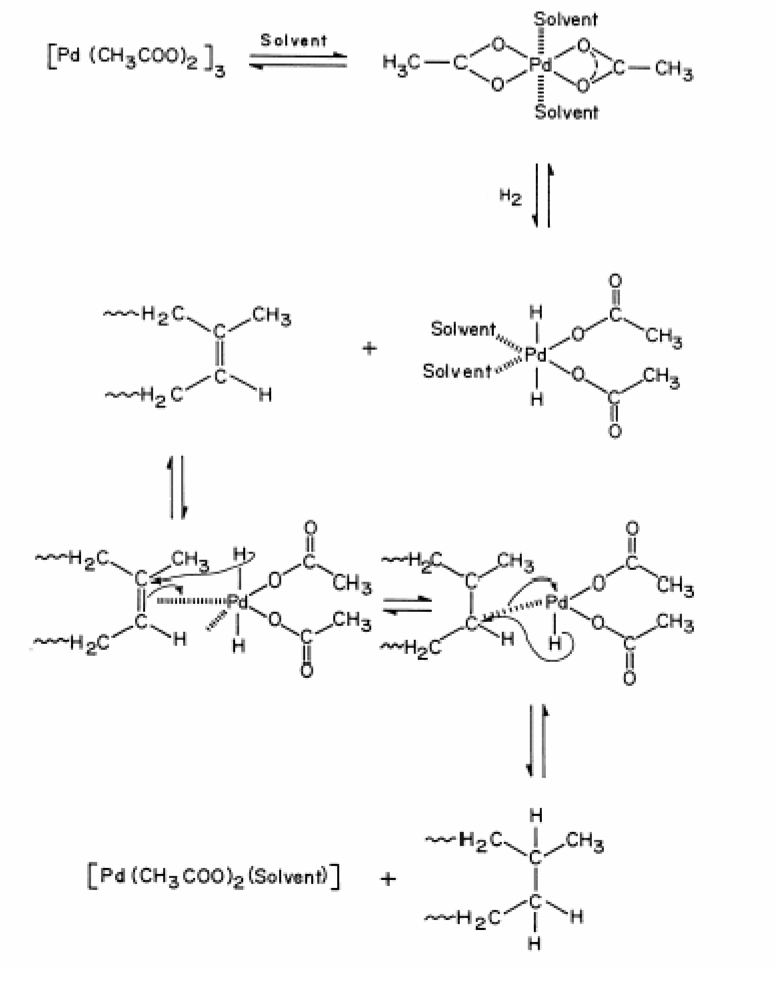


Figure 2.18 Mechanism of hydrogenation of NBR using Pd based catalyst.

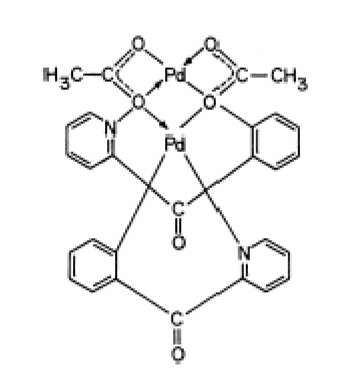


Figure 2.19 Structure of six-membered cyclopalladate complex of 2-benzoylpyridine.

2.6.2 Homogeneous hydrogenation using Ziegler type catalysts

Ziegler type catalysts Ziegler-Natta catalysts [126] consist of a mixture of metal alkyl of Group (I) to (III) metals (known as co-catalyst) and transition metal salts of Group (IV) to (VIII) metals (known as catalyst). Homogeneous Ziegler-type catalysts show high degree of hydrogenation at a relatively moderate temperature and pressure, low catalyst requirement, and reaction time. Hydrogenation of olefins using Ziegler type catalysts based on Co, Cr, and Ti in combination with alkylaluminum co-catalyst was first studied by Breslow [127]. Yakubchik *et al.* [128] first used Ziegler type catalysts for hydrogenation of polymers. Since then Ziegler type catalysts have been extensively used for the hydrogenation of homopolymers and copolymers especially styrene based block copolymers.

The first commercial product hydrogenated using Ziegler-Natta catalyst, namely, ″Kraton G″ (Hydrogenated styrene-butadiene-styrene block copolymer), was introduced by Shell chemical Co., USA in 1970. Over the years a large number of catalysts have been developed to hydrogenate diene homopolymers and copolymers.

Yoshimoto *et al.* [129] hydrogenated SBR in *n*-hexane using Ni(naphthenate)$_2$ and triethylaluminum (TEAL) under 0.35 MPa hydrogen pressure at 80°C for 5.5 h. They hydrogenated SBR also in toluene with the same catalyst [130]. They also used Ni-naphthenate-TEAL and cyclopentadiene complex as catalyst. Bis(1,5-cyclooctadiene) nickel [131], iron-(naphthenate)-TEAL [132] and cobalt(octoate)$_2$-TEAL [133] have been used to hydrogenate SBR. Duck *et al.* [134]

hydrogenated SBR in toluene using bis(3,5-diisopropylsalicylate)nickel(II) and BuLi. They also studied the physical and mechanical properties of hydrogenated SBR (HSBR) which exhibited thermoplastic elastomer (TPE) behavior. Devault and Johnson70 hydrogenated SBR using Ni(octoate)$_2$ and TEAL under relatively reduced reaction conditions. Halasa *et al.* [135] studied the hydrogenation of SBR using cobalt(II) complexes and trialkylaluminium as reducing agents. Molova *et al.* [136] prepared a catalyst by mixing bis(1,3-pentadionate) nickel(II) with sodium bis(2-methoxyethoxy) dihydroaluminate in 1.0:0.5 to 1.0:5.0 molar ratio, for hydrogenation of diene copolymers. A cyclohexane solution of butadiene-styrene block copolymer was hydrogenated with this catalyst for 30 minutes to get 86% reduction of double bonds. Willis [137] studied the hydrogenation of styrene butadiene block copolymer using Ni(octoate)$_2$ and co-catalyst-BuLi as reducing agent (Li/Ni = 6:1). They also hydrogenated carboxylated S-B-S block copolymer using Ni(2-ethylhexanoate)$_2$ and TEAL [138]. Hatsutori *et al.* [139] hydrogenated SBR in cyclohexane using Ni(naphthenate)2-BuLi-THF mixture at 70°C to achieve 95% hydrogenation.

Hexmeier and Slaugh [140] used MAO as reducing agent for the Ziegler type hydrogenation catalyst. They hydrogenated S-B-S triblock copolymer with Ni(2-ethylhexanoate), MAO and TEAL (Al/Ni = 4) under 6.0 MPa and at 90°C to get 95% hydrogenation at 3 h. Ishihara *et al.* [141] carried out hydrogenation of SBR in cyclohexane using Ni(naphthanoate)$_2$ and triisobutyl aluminum (TIBAL) at 70°C under 1.3 MPa hydrogen pressure. They achieved complete hydrogenation in 2 h. Feng *et al.* [142] carried out the selective hydrogenation of S-B-S triblock copolymer in cyclohexane solvent and examined the kinetics of the reaction. The rate of hydrogenation was maximum at Al-Ni molar ratio of 3 and Ni concentration 2.5-7.3 mg/g. The apparent activation energies for hydrogenation at constant and changing pressure were 47.6 kcal/mol and 35.8 kcal/mol respectively.

Singha and Sivaram hydrogenated styrene-isoprene-styrene triblock copolymer in cyclohexane solution using Ni(octoate)$_2$ and TEAL (Al/Ni = 4) as reducing agent. They obtained complete and selective hydrogenation of isoprene segments under 4.0 MPa hydrogen pressure at 80°C. Velichkova *et al.* [143] carried out hydrogenation of styrene-isoprene block copolymers and studied the solution properties of hydrogenated products. Styrene-isoprene block copolymer with different monomer compositions were hydrogenated by using homogeneous catalysts based on various nickel complexes. Nickel acetylacetonate, nickel caproate, and nickel(octoate) in combination with TIBAL showed complete hydrogenation of the polymer at 90-100°C and under 0.25 to 0.30 MPa hydrogen pressure. Hydrogenated product was characterized by IR, ^{1}H-NMR and GPC, viscosity and light scattering. GPC studies showed that there was no change in molecular weights before and after hydrogenation.

Recently, metallocene catalysts have attracted attention because of their high activity and excellent stereospecificity in Ziegler-Natta polymerization [144]. These catalysts have also being used for the hydrogenation of diene homopolymers as well as copolymers. Masubuschi and Kishimoto [145] hydrogenated styrene-butadiene block copolymer in cyclohexane in presence of Cp_2TiCl_2 and MeC_6H_4Li for 2 h to give a white soft thermoplastic elastomer with 99% hydrogenation of diene content. They prepared a new catalyst [146] by mixing bis(cyclopentadienyl)titanium di-*p*-tolyl, naphthenate and THF for the hydrogenation of diene copolymers. S-B block copolymer in cyclohexane solution was hydrogenated at 60°C under 2.0 MPa hydrogen pressure for 3 h to get completely hydrogenated copolymer. They also used zirconocene and hafnocene in combination with BuLi to hydrogenate S-B block copolymers.

Hattori and Kitagawa [147] hydrogenated SBR in presence of ditolyl bis(1,5 cyclopentadienyl)titanium and BuLi under 0.25 MPa hydrogen pressure to obtain complete hydrogenation in 30 minutes. Teramoto *et al.* [148] carried out the hydrogenation of SBR in cyclohexane using dibenzylbis(1,5-cyclopentadienyl) titanium and 2,4-di-tert-butyl-4-methyl phenoxy lithium to achieve complete hydrogenation whereas only 52% hydrogenation could be obtained with co-catalyst BuLi and Cp_2TiCl_2. Hattori and Oshima [149] hydrogenated S-B-S block copolymer in cyclohexane at 80°C using tetrabenzyltitanium and TEAL to obtain 100% conversion whereas only 70% hydrogenation could be obtained using bis(1,5-cyclopentadienyl)diethyl titanium and TEAL. Hattori *et al.* [150] prepared a catalyst by mixing TEAL-BuLi (1:1) Cp2 TiCl2 and tetrafurfuryloxy lithium in cyclohexane. SBR could be hydrogenated (99%) at 50°C in 15 min. Goshima *et al.* [151] prepared a catalyst by mixing SBR with this catalyst at 70°C and under 1.0 MPa hydrogen pressure to get 98% hydrogenation. Hashiguchi *et al.* [152] prepared a catalyst by mixing Cp_2TiCl_2, BuLi, Et_2AlCl and lithium salt of BHT. This catalyst hydrogenated S-B block copolymer completely.

Chamberlin and Gibbler [153] hydrogenated S-B block copolymer with bis(cyclopentadienyl) titanium diethoxide at 170°C and 1.0 MPa hydrogen pressure to obtain 98% hydrogenation for 3 h. S-B-S block copolymers have also been hydrogenated with Cp_2TiR (R = H or allyl)/co-catalyst-BuLi [154] and Cp_2TiCl_2/BzOMe [155]. Very recently Chamberlin *et al.* [156] used metallocene based on actinides [Cp_2SmPh(THF)] in combination with EtMeCHLi to hydrogenate SBS block copolymer. They achieved 81% hydrogenation at 40-80°C for 3.5 h.

The hydrogenation of diene homopolymers and diene-diene copolymers have also been carried out by using Ziegler-Natta catalysts. The hydrogenation of elastomeric 1,4-BR gives a crystalline polyethylene whereas the hydrogenation of BR containing a moderate amount of 1,2 content gives an elastomeric poly(ethylene-*co*-butylene). Upon hydrogenation, 1,4-IR is converted to an alternating copolymer of ethylene and propylene.

Tikhanirov *et al.* [157] studied the hydrogenation of BR with Cr(III)acetylacetonate and TIBAL. It was found that the homogeneous hydrogenation of 1,4-*cis*-BR in solution at concentrations below 0.1% and the hydrogenation of a low molecular weight compound (cyclohexene) are first order with respect to the unsaturated substance. Upon increasing the concentration of polymer, there is a marked change in the nature of the kinetics. Molecular weight of the polymer had an effect on the rate of hydrogenation. For low MW BR, the initial rate was a linear function of the concentration of polymer in solution. But at higher polymer concentrations, the initial rate was practically independent of the molecular weights. Duck *et al.* [158] hydrogenated BR using bis(isopropylsalicylate) nickel-BuLi-ether complex at 40°C under atmospheric pressure to obtain 93% hydrogenation in 4 h. Pendleton *et al.* [159] hydrogenated BR grafted with styrene with $Co(octoate)_2$ and TEAL under 0.3 MPa hydrogen pressure at 75°C for one hour. Duck studied the hydrogenation of BR and the properties of hydrogenated BR. They prepared a catalyst by mixing BuLi and bis(3,5-diisopropyl salicylate) nickel(II) in dry toluene. BR was hydrogenated using this catalyst at 75°C to obtain 96% hydrogenation for 4 h.

Komatsu *et al.* [160] formed the hydrogenation of BR in toluene using bis(cyclooctadiene)nickel(II) and TEAL at 50°C and under 3.0 MPa hydrogen pressure. They obtained 84% hydrogenation in 5 h whereas 50% hydrogenation was achieved without TEAL. Butadiene-isoprene block copolymers were hydrogenated using Ni(octoate)$_2$ and TEAL as reducing agent.[161-164] hydrogenated BR in hexane with caprolactum-CoCl$_2$ complex reduced with TIBAL. He obtained complete hydrogenation at 100°C under 1.3 MPa hydrogen pressure.

Falk [165] studied the hydrogenation of BR and IR using Co(octoate)$_2$ and Ni(octoate)$_2$ in combination with TEAL or BuLi as reducing agent at 50°C and 0.3 MPa hydrogen pressure. The *cis*-1,4-BR was selectively hydrogenated even in presence of *cis*-1,4-IR using Co(octoate)$_2$ and TEAL. This reflects the relative reactivity of a disubstituted and trisubstituted olefin towards hydrogenation using Zeigler type catalysts. Alkyl lithiums [166,167] also can be used as the reducing agent for the hydrogenation of BR or IR. The lithium/cobalt ratio for maximum hydrogenation activity is from 3 to 5. Nickel (II) 2-ethylhexanoate shows an activity similar to cobalt (II) 2-ethylhexanoate. The rate of hydrogenation of 1,4-BR increases with an increase in catalyst concentration at a constant temperature of 50°C and 0.30 MPa hydrogen pressure. The activity of the catalyst depends on the reaction temperature. A minimum temperature of 50°C is required for rapid hydrogenation of 1,4-BR. It is very difficult to hydrogenate an aromatic ring because of its inherent stability towards hydrogenation. Very drastic conditions are required to hydrogenate the phenyl ring of these polymers (6.6 MPa H_2 pressure and temperature up to 300°C).

Yagi and Hatsutori [168] prepared a catalyst by mixing Ni(naphthenate)$_2$, Et_3N, and butadiene. BR was hydrogenated with this catalyst to obtain 69% hydrogenation. Lio *et al.* [169] hydrogenated the polymers obtained from ring opening polymerization of norbornene in toluene using Ni(naphthenate)$_2$ and TEAL under 11.0 MPa hydrogen pressure. Hydrogenation of olefins and polyenes using Ziegler type catalysts based on nickel has been reviewed [170].

The other transition metal catalyst which has been used extensively for Ziegler type hydrogenation catalysts is cobalt. Xie *et al.* [171] synthesized 1,2-1,4-1,2-stereotriblock BR by anionic polymerization. They hydrogenated this polymer using a catalyst composed of cobalt (II) 2-ethylhexanoate and TIBAL at a molar ratio of Al/Co = 3.2. Complete hydrogenation was achieved in 30 minutes under 0.25 MPa hydrogen pressure and at 50°C. Dicyclopentadiene-thylene copolymer [172] as hydrogenated in cyclohexane using Co(octoate)$_2$ and TEAL at 90°C and 7.0 MPa hydrogen pressure in 3 h. Abraham [173] hydrogenated butadiene-vinyl pyridine copolymer in toluene sing Co(neodecanoate)$_2$, $(Me_2N)_3PO$ and TEAL under 6.6 MPa hydrogen pressure at 50°C. braham [174] also hydrogenated hydroxyl terminated BR with Co(neodecanoate)$_2$ and TEAL.

Metallocene catalysts have also been used to hydrogenate BR and IR. Wilson and Stevens [175] carried out the hydrogenation of BR using bis(alkyl substituted cyclopentadienyl)lanthanide based catalysts at 90°C and 3.8 MPa hydrogen pressure. Kato and Kishimoto [176] studied the hydrogenation of BR in cyclohexane using 4-methyl phenyl lithium and Cp_2TiCl_2 under 0.50 MPa hydrogen pressure to achieve 90% hydrogenation in 1 h. They [177] also prepared another type of catalyst by mixing bis(pentamethyl cyclopentadienyl)titanium dichloride and $MgBu_2$ in cyclohexane under 0.2 MPa and 0°C for 15 h. BR was hydrogenated with this catalyst upto 95% under 0.5 MPa hydrogen pressure for 2 h.

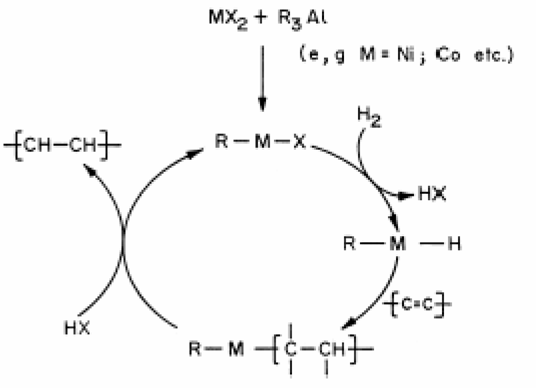


Figure 2.20 Mechanism of hydrogenation of diene elastomers using Ziegler type catalyst.

The mechanism of hydrogenation using Zeigler catalysts involves the formation of lower valent hydrides of transition metal salts as active hydrogenation catalysts (**Figure 2.20**).

The salient features of the catalytic hydrogenation of polymers using Zeigler type catalysts are as follows:

(i) Mono substituted olefins are preferentially hydrogenated compared to the disubstituted olefins, because the rate of insertion of the metal hydride (**Figure2.20**) into the monosubstituted olefin is more facile. The rate of hydrogenation varies in the order:

1,2-BR > 1,4-BR > 1,4-IR

The Z/M [Z = Al or Li, M = Ni or Co etc.,] ratio range for maximum hydrogenation activity is between 3 and 5.

(ii) Molecular weight affects the kinetics of the hydrogenation. For very high MW polymers the kinetics of the reaction is more complicated beyond a particular concentration of the solution. This can be understood in terms of super molecular structures influencing the course of the reaction.

It should be noted that Ziegler-type catalysts are not suitable for those polymers which possess a polar functional group (because of its highly coordinating nature) *e.g.* acrylonitrile-butadiene copolymer (NBR) (known as nitrile rubber).

2.7 Hydrogenation of Natural Rubber

Shahab and Basheer [178] carried out hydrogenation of NR and BR using Pd on $CaCO_3$ at room temperature and atmospheric pressur for several days. The hydrogenation proceeds rapidly in the initial stage of the reaction but slows down considerably in the latter stage. To study the properties of amorphous as well as crystallizable polymers Rachapudy *et al.* [179] hydrogenated BR using nickel-kieselguhr as well as Pd on $CaCO_3$. The palladium catalysts (temperature 70°C, pressure 3.3 MPa) required milder reaction condition relative to the nickel catalyst (temperature 160°C, pressure 5 MPa).

Natural rubber (NR) as well as *cis*- and *trans*-1,4-IR can also be hydrogenated using $RhCl(PPh_3)_3$ as catalyst. Shahab and Baseer [178] hydrogenated NR in benzene using $RhCl(PPh_3)_3$. They achieved only 25% hydrogenation at 65°C in 12 h. Singha reported quantitative hydrogenation of NR using $RhCl(PPh_3)_3$. Complete hydrogenation of NR leads to an alternate copolymer of ethylene and propylene which is very difficult to prepare by conventional polymerization. The reaction kinetics is similar to that obtained for BR.

Natural rubber (NR) also has a very low rate of hydrogenation presumably because of trisubstituted nature of the olefinic unsaturation. As expected BR has a higher hydrogenation rate. Since the activation energy of the hydrogenation of NBR using Pd catalysts is very low, it has a higher rate of hydrogenation.

Nishio [180] studied the homogeneous hydrogenation of NR in toluene solution. The obtained hydrogenated NR shows the elastic material properties comparable to ethylene-propylene copolymer. The hydrogenated NR showed an outstanding improvement of abrasion and anti-ozone properties after hydrogenation reaction.

Tangthongkul [181] carried out hydrogenation of NR with $Ru[CH=CH(Ph)]Cl(CO)(PCy_3)_2$ as a catalyst. They reported that the quantitative hydrogenation of NR can be achieved with $Ru[CH=CH(Ph)]Cl(CO)(PCy_3)_2$ as the catalyst. The presence of impurities and the high molecular weight of NR may reduced the efficiency of the catalyst. The addition of a small amount of acid, that is, *p*-TsOH, appears to neutralize the poisonous effect of the system. The hydrogenation reaction leads to an increase in the thermal stablity of NR without affecting its T_g.

Mahittikul [182] studied hydrogenation of NR latex in the presence of $OsCl(CO)(O_2)(PCy_3)_2$ in chlorobenzene. They found that the hydrogenation reaction showed a first-order dependence on catalyst concentration, inverse order dependence on rubber concentration and second-order to zero-order dependence on hydrogen pressure. The hydrogenation rate was dependent on reaction temperature. Activation energy for this process was 56.79 kJ/mol.

Hinchiranun and cowokers [183] studied hydrogenation of PCIP and NR catalyzed by $[Ir(COD)py(PCy_3)]PF_6$. They found that the hydrogenation of both rubbers exhibited a first-order dependence on hydrogen pressure and a first-to-zero-order dependence with respect to the catalyst concentration. The apparent activation energy for the hydrogenation of CPIP and NR was found to be 79.8 and 75.6 kJ/mol, respectively. The increase in the degraded temperature of the hydrogenated rubber prodducts demonstrated that hydrogenation increased the thermal stability of CPIP and NR without affecting T_g .

Hinchiranun [184] carried out hydrogenation of NR in the presence of $OsHCl(CO)(O_2)(PCy_3)_2$. They found that the rate of hydrogenation reaction was first order with respect to catalyst concentration and hydrogen pressure. The hydrogenation rate was dependent on reaction temperature, and the activation energy was 122.76 kJ/mol.

Mahittikul [185] studied non-catalytic hydrogenationof natural rubber latex. They found that a ratio 2 mol of TSH/1 mol of C=C provided >90% hydrogenation. The diimide hydrogenation method provided the viable process to improve the thermal stability of NR latex without affecting it glass transition temperature.

2.8 Scope of Present Thesis

One of the problems that can cause the difficulty of hydrogenation of rubber in latex state is the presence of high content of non-rubber components in rubber latex such as proteins as know that the rubber particle is covered with protein layers, which acted as the impurity in the rubber latex. In order to reduce the effect impurity, thus, it is necessary to remove these proteins from rubber particle by enzymatic deproteinization to get deproteinized NR latex or DPNR latex and this DPNR-latex is then expected to be applicable to use as starting material for hydrogenation reaction in the present work.

The scope of this work is divided into two parts. The first part was an attempt to investigate the hydrogenation reaction of DPNR latex by using $Pd(OAc)_2$ as a catalyst. This part includes a method to prepare the catalyst solution in laboratory.

The second part was studied the effect of %DRC of DPNR, the catalyst concentration, H_2 pressure, reaction time, and temperature on hydrogenated DPNR.

CHAPTER III

MATERIALS AND METHODS

3.1 Chemicals

The chemicals used in this study are listed in **Table 3.1**. Toluene was distilled before use, while other chemical substances were used as received.

Table 3.1 Chemicals used in this study

Chemical	Supplier	Grade
Acetone	Fluka	Commercial
Chloroform	Lab Scan	AR
Chloroform-d	Aldrich	AR
Dimethylglyoxime	Sigma-aldrich	AR
Fresh natural rubber latex	Thai Rubber Latex Co, Ltd	Commercial
Palladium (II) acetate	Fluka	AR
Polyvinylpyrrolidone K30	Fluka	AR
Potassium hydroxide	BDH	AR

Table 3.1 Chemicals used in this study (Continued)

Chemical	Supplier	Grade
Proteolytic enzyme (KP 3939)	KaO	AR
Sodium dodecyl sulphate	BDH	AR
Tetrahydrofuran	Lab Scan	HPLC
TMS	Aldrich	AR
Toluene	Fluka	Commercial
Triton X®-100	BDH	AR

3.2 Apparatus

The apparatus used in this study are listed in **Table 3.2**.

Table 3.2 Apparatus used in this study

Instrument	Supplier / Trade mark
Constant Temperature bath	NESLAB Instruments: Model GP-300D
DSC	Perkin-Elmer: DSC-7
FT-IR Spectrophotometer	JASCO: FT-IR SA 450

Table 3.2 Apparatus used in this study (Continued)

Instrument	Supplier / Trade mark
Magnetic Stirrer	Thermolyne
NMR Spectrophotometer	BRUCKER: DTX 300
Oven	MEMMERT
Pressure reactor	Parr Instruments: Model Parr 4842
TGA	Mettle Toledo TGA/SDTA 8^{15e}
Ubbelodhe Viscometer	SCHOTT: Model 531 110
Vacuum Oven	EYELA: VOS 451-SD
Windy Oven	EYELA: WFO-1001SD

3.3 Natural Rubber (NR) Latex

3.3.1 Determination Dry Rubber Content (%DRC)

$$\%DRC = \frac{W_x}{W_t} \times 100$$

where, W_x = weight of dried coagulum (g)

W_t = weight of NR latex sample (g)

3.3.2 Preparation of Deproteinized natural rubber (DPNR)

Fresh natural rubber (NR) latex having 30% dry rubber content (DRC), which was provided from Thai Rubber Latex Co, Ltd., was added with 1% w/v of sodium dodecyl sulphate (SDS) and 0.04% w/v of proteolytic enzyme (*KP3939*, Kao Co.). The latex was incubated at 37^{o}C for 12 h, followed by ultracentrifugation at 13,000 rpm for 30 min. The cream fraction was redispersed with 1% w/v of SDS to make 30% DRC latex and recentrifuged to make 55% DRC latex. After deproteinization was completed, the DPNR latex was stored in a refrigerator at below 10^{o}C

3.4 Hydrogenated deproteinized natural rubber (HDPNR)

3.4.1 Preparation of catalyst solution

$Pd(OAc)_2$ mixed with HNO_3 and then added H_2O and polyvinylpyrrolidone. The mixture was stirred for 20 min and adjusted to pH 9.0 by 1% KOH. The catalyst solution was used in next step.

3.4.2 Preparation HDPNR

DPNR latex was mixed with catalyst solution. The mixture was stirred for 20 min under nitrogen and then transferred to the Parr hydrogenation apparatus where the mixture was purged two times with hydrogen, before filling to the required pressure. During the course of hydrogenation the mixture was agitated by stirring. Hydrogenation was carried out at elevated temperatures.

HDPNR latex adjusted to pH 9.5 after that added dimethylglyoxime into the mixture. Heated to 80ºC for 5 h. and then filtered, centrifuged the solution part at 8000 rpm for 30 min. The solution was coagulated with acetone and dried in vacuum at 50ºC overnight.

3.4.2.1 Effect of %dry rubber content (DRC)

The various %DRC of DPNR (10, 20 and 30% DRC) latex was mixed with 0.0042 M catalyst solution. The mixture was stirred for 20 min under nitrogen and then transferred to the Parr hydrogenation apparatus where the mixture was purged two times with hydrogen, before filling to 3 MPa H_2 pressure. During the course of hydrogenation the mixture was agitated by stirring. Hydrogenation was carried out at 50°C for 6 h. The same procedure as given in section 3.4.2 was carried out.

3.4.2.2 Effect of ratio (catalyst/rubber)

DPNR latex was mixed with various ratios between catalyst and rubber particle (0.0067, 0.0133, 0.0100, 0.0200, 0.0300, 0.0400 and 0.0600). The mixture was stirred for 20 min under nitrogen and then transferred to the Parr hydrogenation apparatus where the mixture was purged two times with hydrogen, before filling to 3 MPa H_2 pressure. During the course of hydrogenation the mixture was agitated by stirring. Hydrogenation was carried out at 50°C for 6 h. The same procedure as given in section 3.4.2 was carried out.

3.4.2.3 Effect of hydrogen pressure

10% DRC of DPNR latex was mixed with 0.0042 M catalyst solution. The mixture was stirred for 20 min under nitrogen and then transferred to the Parr hydrogenation apparatus where the mixture was purged two times with hydrogen, before filling to the required pressure (1, 3, 5 and 7 MPa). During the course of hydrogenation the mixture was agitated by stirring. Hydrogenation was carried out at 50°C for 6 h. The same procedure as given in section 3.4.2 was carried out.

3.4.2.4 Effect of temperature

10% DRC of DPNR latex was mixed with 0.0042 M catalyst solution. The mixture was stirred for 20 min under nitrogen and then transferred to the Parr hydrogenation apparatus where the mixture was purged two times with hydrogen, before filling to 3 MPa H_2 pressure. During the course of hydrogenation the mixture was agitated by stirring. Hydrogenation was carried out at various temperatures (25, 50, 75 and 100°C) for 6 h. The same procedure as given in section 3.4.2 was carried out.

3.4.2.5 Effect of reaction time

10% DRC of DPNR latex was mixed with 0.0042 M catalyst solution. The mixture was stirred for 20 min under nitrogen and then transferred to the Parr hydrogenation apparatus where the mixture was purged two times with hydrogen, before filling to 3 MPa H_2 pressure. During the course of hydrogenation the mixture was agitated by stirring. Hydrogenation was carried out at 50°C for various time (1, 2, 4 and 6 h.). The same procedure as given in section 3.4.2 was carried out.

3.5 Characterization of HDPNR

3.5.1 Determination of gel content

The rubber sample dissolved in distilled toluene at a concentration 0.1% w/v was kept in the dark without stirring for one week at room temperature. The solution was centrifuged at 8,000 rpm for 20 min to separate the gel fraction from the sol fraction. The precipitated gel fraction was recovered by coagulation with methanol and dried in *vacuo* at room temperature. The gel content was calculated from the percent between weight ratio of gel and original rubbers.

3.5.2 NMR measurement

The structural changing of natural rubber by hydrogenation process was confirmed by quantitative measurement of *cis*-isoprene units using ^{1}H-NMR. Tetramethylsilane (TMS) was added to rubber as internal standard of the intensity at 0 ppm. The intensity of =CH proton signal at 5.1 ppm was analyzed by comparison with the signal from saturated proton, which is around 0.84 ppm under conditions as shown in **Table 3.3**.

Table 3.3 Conditions for ^{1}H-NMR measurement

Parameters	Condition
Rubber concentration	2.0% w/v
Solvent	$CDCl_3$
Temperature	50°C
Observed frequency	300 MHz
Sweep width	4,000 MHz
Number of scans	500-1,000 scans

3.5.3 Determination of percentage of hydrogenation

$$\text{Percentage of hydrogenation} = \left(\frac{I_{0.84}}{3(I_{5.2}) + I_{0.84}} \right) \times 100$$

Where $I_{0.84}$ = Resonance intensity of ^{1}H-NMR spectrum at chemical shift of 0.84 ppm

$I_{5.2}$ = Resonance intensity of ^{1}H-NMR spectrum at chemical shift of 5.2 ppm

3.5.4 Differential Scanning Calorimetry (DSC)

DSC is the technique that measures the changes in energy inputs supplied directly into a sample and a thermally inert reference while both sample and reference are subjected to a controlled temperature programmed. In other words, DSC measures directly the amount of heat absorbed or released by a sample as it is heated, cooled or held isothermally (at a constant temperature). For thermal events that can be studied using DSC, these include glass transition temperature (T_g), specific heat, degree of crystallization and crystallization kinetics, curing kinetics, melting and heat of melting, oxidation, compositional difference in blends, decomposition and polymorphism.

DSC (Perkin Elmer DSC-7) was employed in this project to study the glass transition temperature (T_g) polyisoprene and hydrogenate products. About 20 - 30 mg. of each sample was weight accurately and placed in 50 μl aluminium pans. The sample was scan from -100 to 20°C at a rate of 20°C/min. Resulting thermograms were recorded and processed by computer software.

3.5.5 Thermogravimetric Analysis (TGA)

TGA measures the change in mass of a sample as it is heated cooled or held isothermal (at a constant temperature). Causes of the change in mass may be from degradation of sample, volatile substrate or moisture within sample. TGA can detect percentage of moisture and volatile, percentage of fillers and additives in multi-component system, degradation temperature, composition difference in blends and decompositional kinetics.

Thermal stability of hydrogenated samples was studied using a Thermogravimetric Analyzer (Perkin Elmer TGA-7). The experiment was carried out under nitrogen atmosphere, and the sample weight was approximately 10 -20 mg. The sample was initially heated from 50°C to approximately 650°C at a scanning rate of 20°C/min. The TGA thermograms were recorded using PC software.

3.5.6 Fourier-transform infrared (FT-IR) spectrometry

The HDPNR solution was cast onto a KBr disc. The solution film analyzed by FT-IR spectrophotometer (JASCO: FTIR-460 plus) at a resolution of 4 cm^{-1} with 100 scans.

3.5.7 Determination of intrinsic viscosity, viscosity-average molecular weight and Huggins' *k'* constant by viscometry

Intrinsic viscosity was measured with a single bulb Ubbelohde viscometer (SCHOTT, CT52) at 30±0.01°C in distilled toluene. Viscosity-averate molecular weight was calculated by Mark-Houwink's equation. The Mark-Houwink constant, K, used in this calculation was 33.1 x 10^{-5} and a constant was 0.71 [186].

The Huggins' constant (*k'*) was calculated using the following equations:

$$[\eta] = 33.1\times10^{-5} M_v^{0.71} \qquad (1)$$

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \qquad (2)$$

Where, η_{sp}/c, $[\eta]$, c, M_v and k' represent the reduced viscosity, intrinsic viscosity, concentration expressed as g/dl, viscosity-average molecular weight and Huggins' constant, respectively.

3.6 Condition of HDPNR

HDPNR I is prepared by hydrogenation of 30% DRC of DPNR latex, the amount of catalyst 0.2 g (ratio (catalyst/rubber particle = 0.0067) under 3 MPa H_2 pressure at 50°C for 6 h.

HDPNR II is prepared by hydrogenation of 30% DRC of DPNR latex, the amount of catalyst 0.4 g (ratio (catalyst/rubber particle = 0.0133) under 3 MPa H_2 pressure at 50°C for 6 h.

HDPNR III is prepared by hydrogenation of 30% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0200) under 3 MPa H_2 pressure at 50°C for 6 h.

HDPNR IV is prepared by hydrogenation of 20% DRC of DPNR latex, the amount of catalyst 0.2 g (ratio (catalyst/rubber particle = 0.0100) under 3 MPa H_2 pressure at 50°C for 6 h.

HDPNR V is prepared by hydrogenation of 20% DRC of DPNR latex, the amount of catalyst 0.4 g (ratio (catalyst/rubber particle = 0.0200) under 3 MPa H_2 pressure at 50°C for 6 h.

HDPNR VI is prepared by hydrogenation of 20% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0300) under 3 MPa H_2 pressure at 50°C for 6 h.

HDPNR VII is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.2 g (ratio (catalyst/rubber particle = 0.0200) under 3 MPa H_2 pressure at 50°C for 6 h.

HDPNR VIII is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.4 g (ratio (catalyst/rubber particle = 0.0400) under 3 MPa H_2 pressure at 50°C for 6 h.

HDPNR IX is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 3 MPa H_2 pressure at 50°C for 6 h.

HDPNR X is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 3 MPa H_2 pressure at 25°C for 6 h.

HDPNR XI is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 3 MPa H_2 pressure at 75°C for 6 h.

HDPNR XII is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 3 MPa H_2 pressure at 100°C for 6 h.

HDPNR XIII is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 1 MPa H_2 pressure at 50°C for 6 h.

HDPNR XIV is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 5 MPa H_2 pressure at 50°C for 6 h.

HDPNR XV is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 7 MPa H_2 pressure at 50°C for 6 h.

HDPNR XVI is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 3 MPa H_2 pressure at 50°C for 1 h.

HDPNR XVII is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 3 MPa H_2 pressure at 50°C for 2 h.

HDPNR XVIII is prepared by hydrogenation of 10% DRC of DPNR latex, the amount of catalyst 0.6 g (ratio (catalyst/rubber particle = 0.0600) under 3 MPa H_2 pressure at 50°C for 4 h.

CHAPTER IV
RESULTS AND DISCUSSIONS

4.1 Preparation of hydrogenated deproteinized natural rubber latex

In this present work, we focused on hydrogenation reaction of DPNR latex by using $Pd(OAc_2)_2$ as a catalyst .

4.1.1 Study of some effect on hydrogenation

4.1.1.1 Effect of %dry rubber content (DRC)

The effect of %DRC has been studied at 50°C, under 3 MPa hydrogen pressure, ratio (catalyst/rubber particle) 0.0067-0.0600 and time period of 6 h.

Figure 4.1 shows the relationship between ratio (catalyst/rubber) and %hydrogenation as various %DRC, H_2 pressure = 3 MPa, time = 6 h, and temperature = 50°C.

It is clear from this figure that an increase in the %DRC, increase rubber concentration, caused a reduction in the percentage of hydrogenation. It is likely that the active catalyst species was not adequate for carbon-carbon double bonds in the system, and thus, the percentage of hydrogenation declined with increasing rubber concentration Since rubber solution ay high rubber concentration was more viscous than that at low rubber concentration, it was possible that for the high rubber concentration system, it was difficult for the catalyst species to react with carbon-carbon double bond in the rubber structure, and thus, the percentage of hydrogenation was decreased as same result from Mahittikul et al. [182].

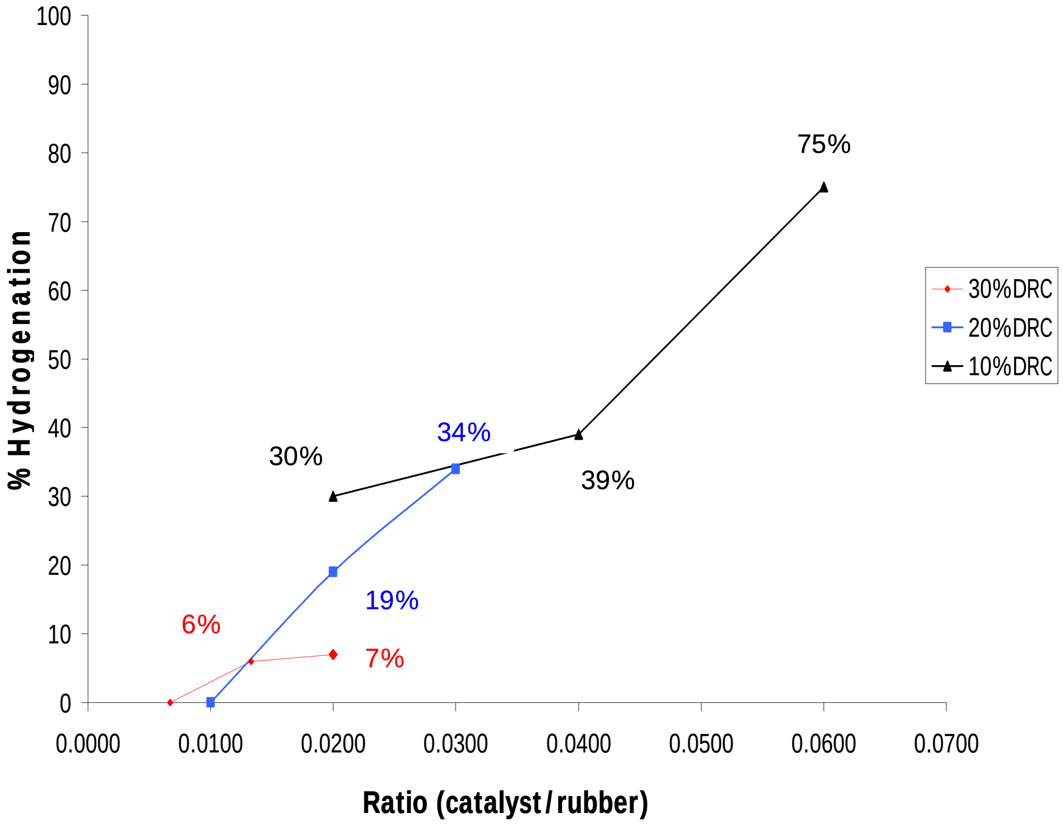


Figure 4.1 The relationship between ratio (catalyst/rubber) and percentage of hydrogenation as various %DRC at 50°C for 6 h under H_2 pressure of 3 MPa

It is concluded that 10% DRC of DPNR show the higher percentage of hydrogenation than 20% and 30% DRC.

The ratio (catalyst/rubber) at 0.0200 showed three point of percentage of hydrogenation of HDPNR, it is presented the three %DRC of DPNR. 10% DRC showed the higher percentage of hydrogenation than that 20% and 30% DRC.

4.1.1.2 Effect of the ratio (catalyst/rubber)

The effect of the ratio (catalyst/rubber) has been studied at 50°C, under 3 MPa hydrogen pressure and time period of 6 h.

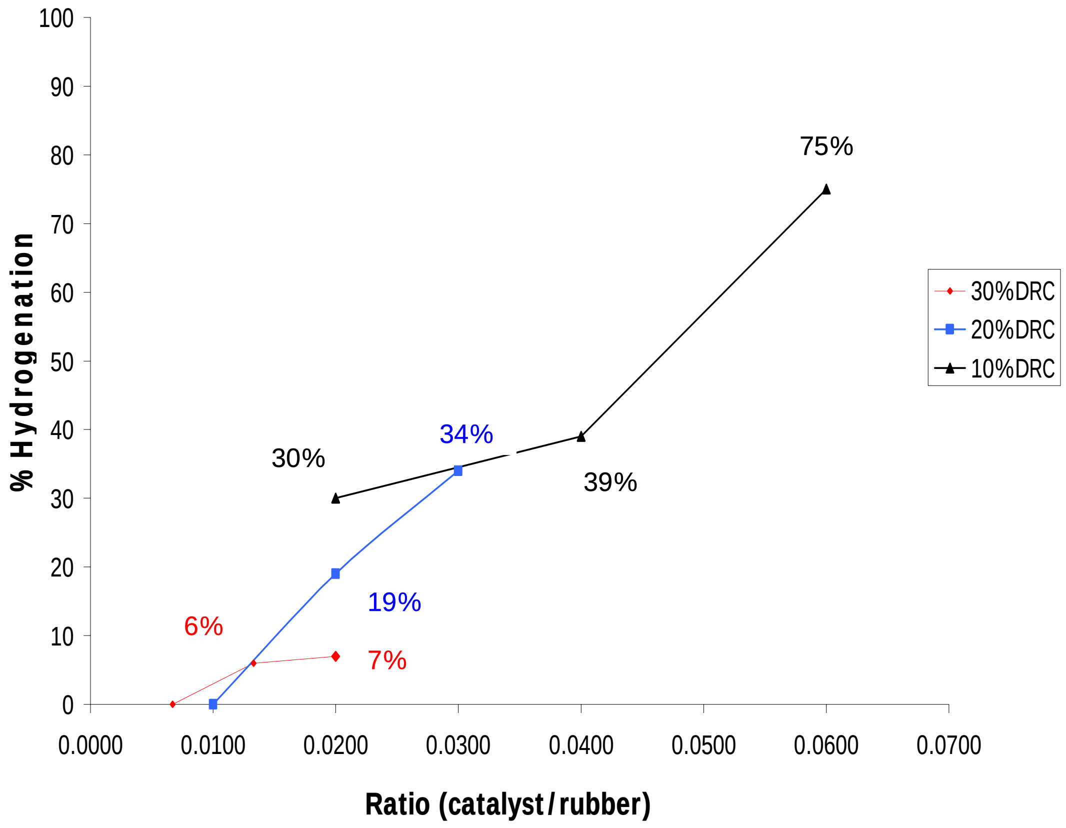


Figure 4.2 The relationship between ratio (catalyst/rubber) and percentage of hydrogenation as various %DRC at 50°C for 6 h under H_2 pressure of 3 MPa

Figure 4.2 shows Relationship between ratio (catalyst/rubber) and percentage of hydrogenation as various %DRC at 50°C for 6 h under H_2 pressure of 3 MPa. It can be seen from this figure that percentage of hydrogenation increases with increasing ration (catalyst/rubber). It indicated that the active species is linearly proportional to catalyst precursor loading. This observation is consistent with the work of Mahittikul et al. [182]. At ratio (catalyst/rubber) 0.0600 showed the highest percentage of hydrogenation.

It can be seen that an increased ratio (catalyst/rubber) increases the percentage of hydrogenation, not affect of %DRC of HDPNR

4.1.1.3 Effect of H_2 pressure

The effect of H_2 pressure has been studied at ratio (catalyst/rubber) 0.0600, temperature 50°C for 6 h.

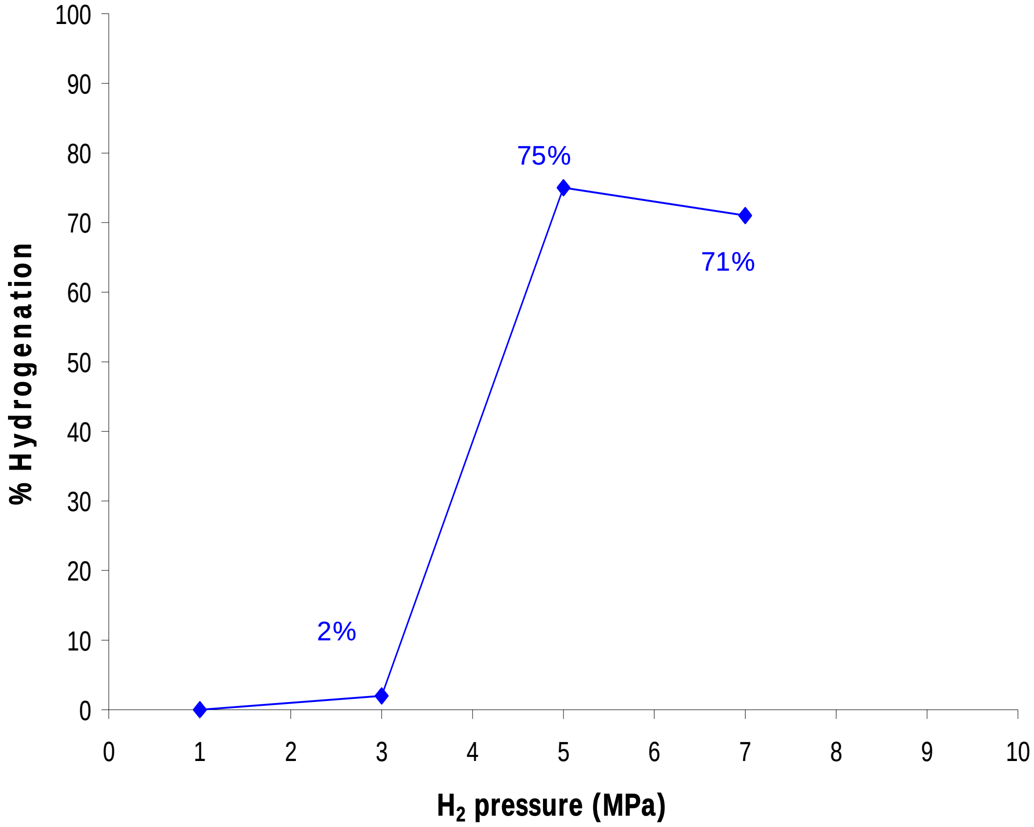


Figure 4.3 The relationship between hydrogen pressure and percentage of hydrogenation at ratio (catalyst/rubber) 0.0600, 50°C for 6 h under various H_2 pressures

Figure 4.3 shows the relationship between hydrogen pressure and percentage of hydrogenation at ratio (catalyst/rubber) 0.0600, 50°C for 6 h under various H_2 pressures. It can be seen from this figure that the rate of DPNR hydrogenation exhibited first order with respect to the hydrogen pressure 1, 3 and 5

MPa and then shifted toward zero order dependence when the hydrogen pressure was 7 MPa. In addition, for NBR hydrogenation in the presence of $RhCl(PPh_3)_3$ system, it was found that the order of reaction with respect to hydrogen pressure shifted from a first- to zero-order behavior with increasing hydrogen pressure [187]. However, the hydrogenation of diene polymer, such as NBR [188] and PIP [189], catalyzed by $OsHCl(CO)(O_2)(PCy_3)_2$ was found to exhibit a second-order dependence on the hydrogen pressure, which then tended to a zero-order behavior at high hydrogen pressure.

4.1.1.4 Effect of temperature

The effect of temperature has been studied at ratio (catalyst/rubber) 0.0600 under 3 MPa hydrogen pressure for 6 h.

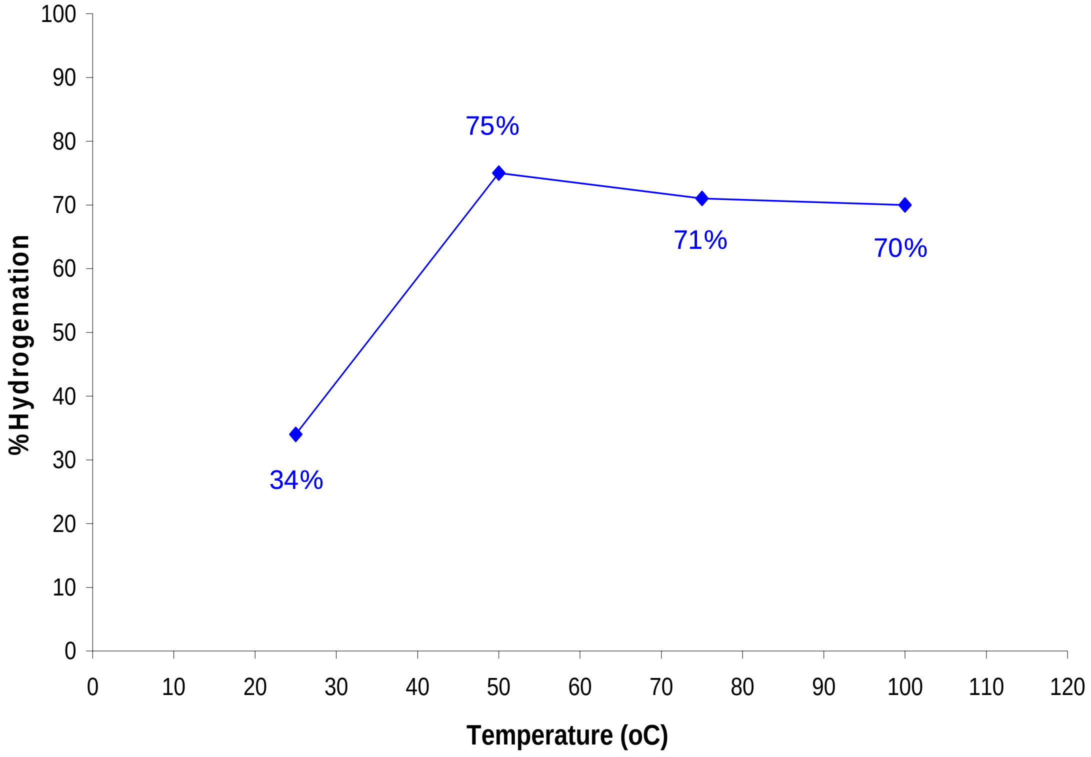


Figure 4.4 The relationship between temperature and percentage of hydrogenation at ratio (catalyst/rubber) 0.0600 under H_2 pressure of 3 MPa for 6 h

Figure 4.4 shows the relationship between temperature and percentage of hydrogenation at ratio (catalyst/rubber) 0.0600 under H_2 pressure = 3 MPa for 6 h. It can be seen from this figure that until the temperature over 50°C, i.e. 75 and 100°C, the percentage of hydrogenation slightly decreased.

4.1.1.5 Effect of reaction time

The effect of reaction time has been studied at 50°C, under 3 MPa hydrogen pressure, ration (catalyst/rubber) 0.0600.

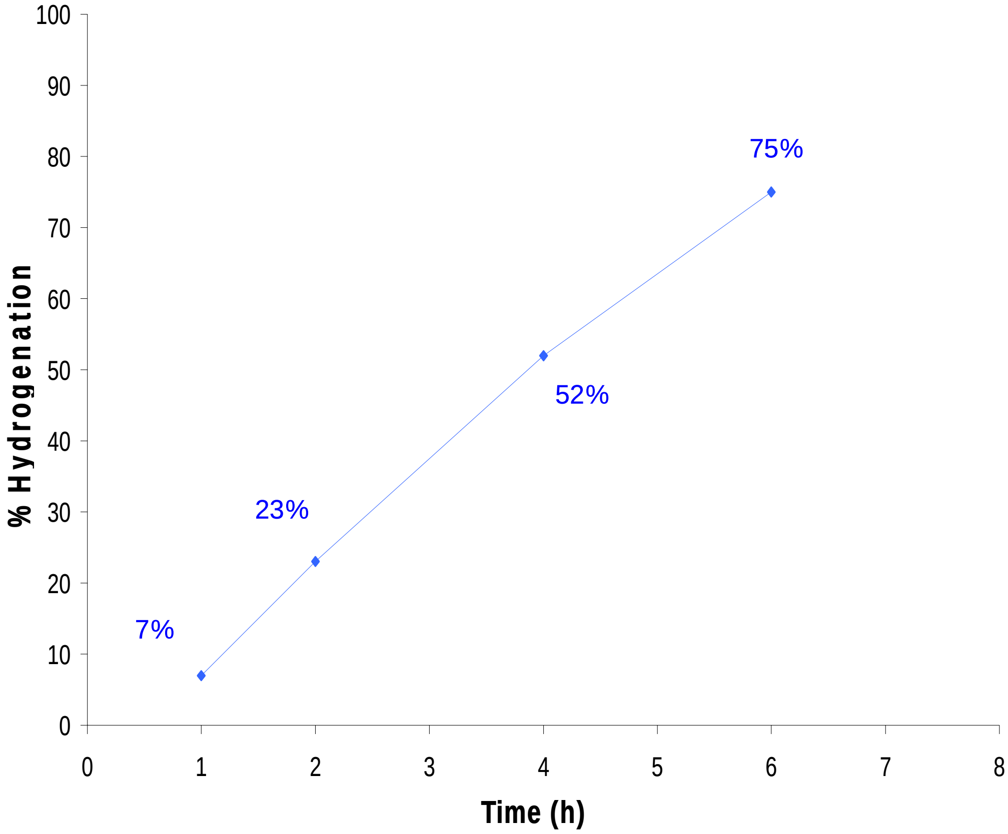


Figure 4.5 The relationship between time and percentage of hydrogenation at 10%DRC of DPNR, [Pd] = 0.0042 M, under H_2 pressure = 3 MPa and at 50°C

Figure 4.5 shows the relationship between time and percentage of hydrogenation at ratio (catalyst/rubber) 0.0600 under H_2 pressure = 3 MPa at 50°C. It can be seen from this figure that percentage of hydrogenation increases with increasing reaction time. This may be due to the rubber particle has enough time to react with catalyst at longer reaction time, resulting in high percentage of hydrogenation, *vice versa*. A maximum of 75% hydrogenation is obtained at 6 h reaction time.

4.1.2 Structural characterizations of HDPNR

4.1.2.1 Fourier Transforms Infrared Spectroscopy (FT-IR)

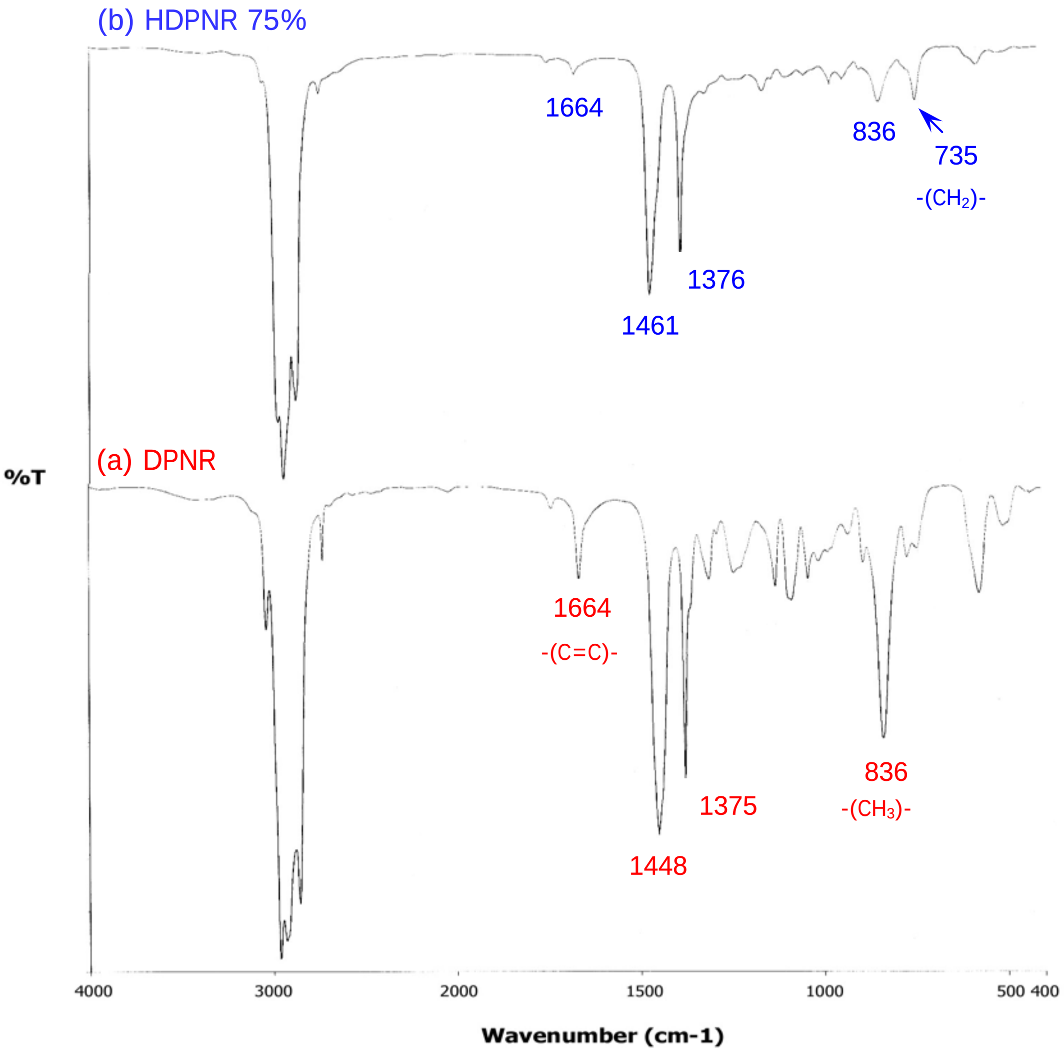


Figure 4.6 FTIR spectrums of (a) DPNR and (b) HDPNR (75% hydrogenation)

FTIR spectra of (a) DPNR and (b) HDPNR are depicted in **Figure 4.6.** The FTIR spectra of DPNR exhibits two important characteristic peaks at 1,664 and 836 cm^{-1}, attributing to the C=C stretching mode and the C-H out of plane deformation of the trisubstituted olefinic of polyisoprene, respectively. As the hydrogenation reaction process, the intensity of the peaks at 1,664 and 836 cm^{-1} are gradually decreased. Moreover, the appearance of peak at 735 cm^{-1}, assigned to the $–(CH_2)–$ groups of the hydrogenated products, is clearly observed.

4.1.2.2 ^{1}H-NMR spectroscopy

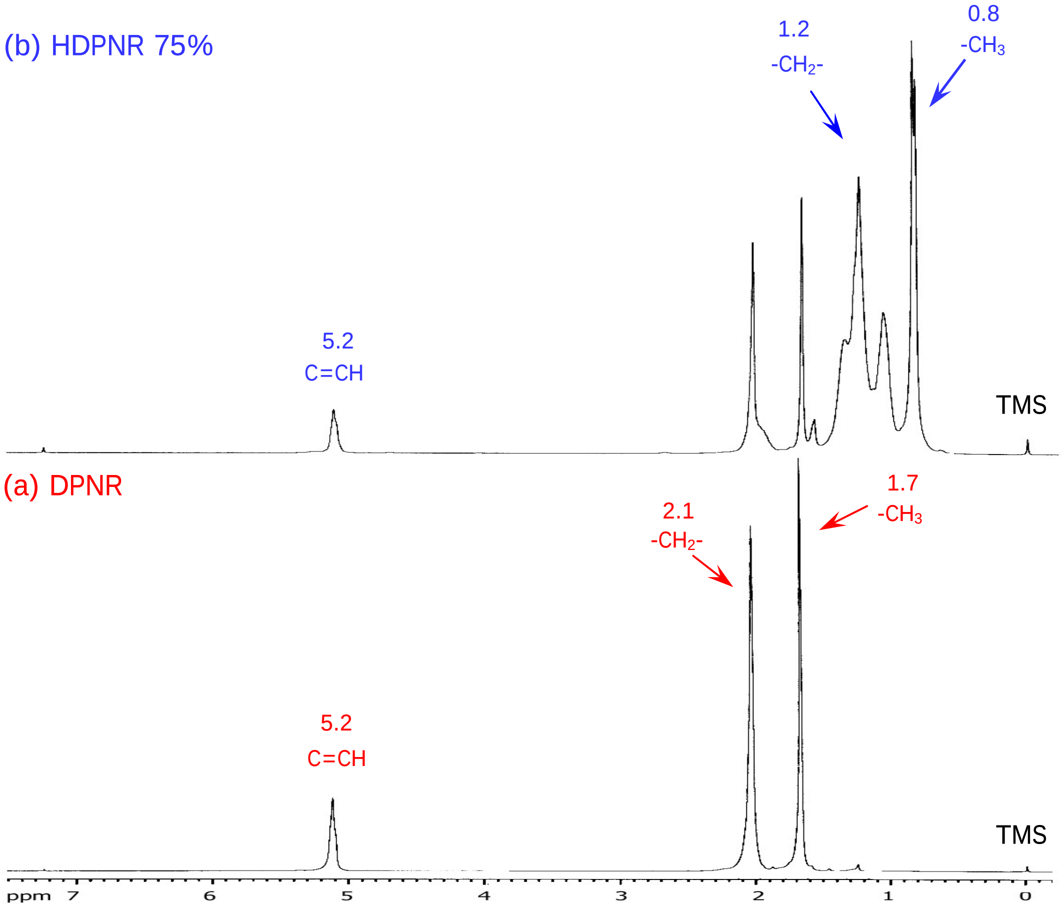


Figure 4.7 ^{1}H-NMR spectra of (a) DPNR and (b) HDPNR (75% hydrogenation)

The microstructure of HDPNR can be investigated by ^{1}H-NMR measurement as the signal of the proton adjacent to the double bond decreases as the hydrogenation proceeds.

Figure 4.7 (a) and (b) shows the ^{1}H-NMR spectra of DPNR and HDPNR, respectively. It can be seen that the 1H-NMR spectra of DPNR shows signals at 1.75, 2.12 and 5.25 ppm, which are attributed to –CH3, -CH2- and olefinic protons, respectively.

After hydrogenation, the peak at 5.25 ppm drastically decreases and the appearance of the signal at 0.8 and 1.1 – 1.3 ppm, which are assigned to methyl and methylene protons of the saturated unit, in **Figure 4.7 (b**) confirms the occurrence of hydrogenation reaction. The integrated areas of the signal at 5.2 and 0.8 ppm, corresponding to the olefinic unit and methyl proton of saturated unit, respectively, were used for the determination of the percentage of hydrogenation.

Based on this result, it can be deduced it is high potential to prepare hydrogenated NR in the latex state.

4.1.2.3 ^{13}C-NMR spectroscopy

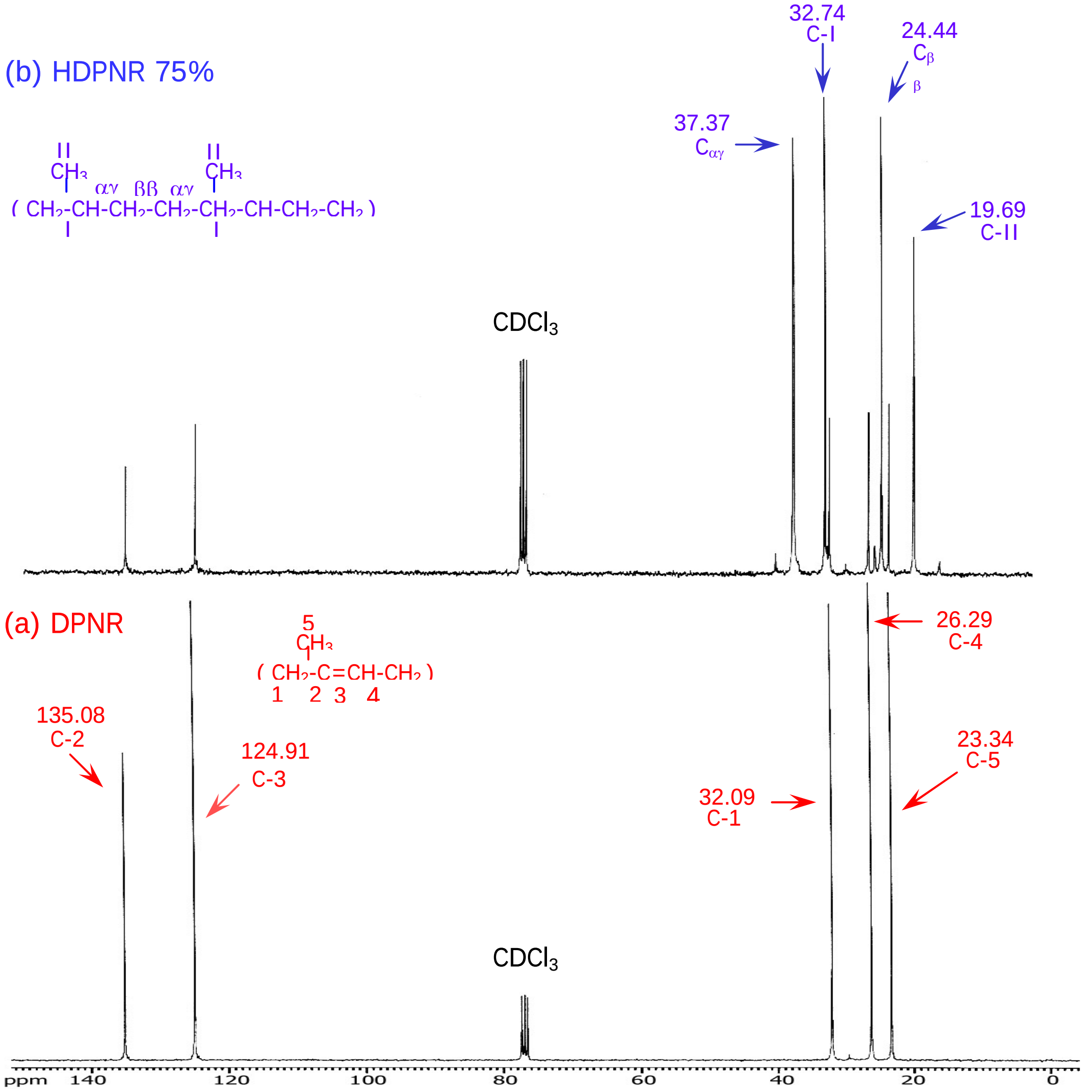


Figure 4.8 ^{13}C-NMR spectrums of (a) DPNR and (b) HDPNR (75% hydrogenation)

^{13}C-NMR spectra of (a) DPNR and (b) HDPNR are shown in **Figure 4.8**, respectively. Isoprene unit rubber chain consists of 5 carbon atoms as indicated in Figure 4.8 (a). The C1 methylene carbon is resonated at 32.09 ppm, while the C2 and C3 carbons are appeared at around 135.08 and 124.91 ppm, respectively. Methylene and methyl carbon of C4 and C5 are observed at 26.29 and 23.34 ppm, respectively.

The additional signals at 19.69, 24.44, 32.74 and 37.37 ppm were detected in the HDPNR sample. These signals correspond to the carbon of the methyl, methylene and methane of saturated unit. The carbon signals of the *cis* structure are positioned at 135.08 and 124.91 ppm.

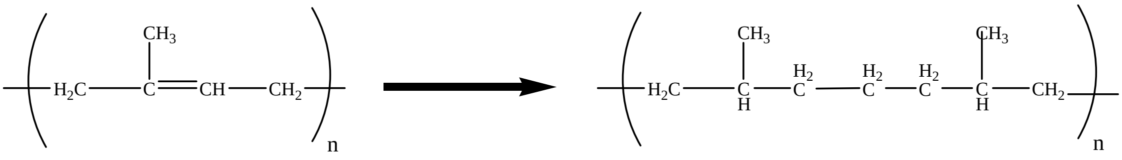


Figure 4.9 The structure from DPNR to HDPNR

4.1.3 Thermal Analysis

It has been known that dienic polymers cannot resist high temperature treatment because their unsaturations in the molecular structure could initiate degradation reaction. In the case of NR, the modification by hydrogenation reaction should increase the thermal stability of the modified product as the degree of unsaturation decreased. Thermal behavior of hydrogenated NR was analyzed using TGA and DSC techniques.

4.1.3.1 Differential Scanning Calorimetry (DSC)

DSC was use to determine glass transition temperature ($T_{g)}$ of hydrogenated rubber. T_g is the temperature at which the amorphous domains of a polymer take on the characteristic properties of the glassy state: brittleness, stiffness, and rigidity. This way determined from the midpoint of the baseline shift of the DSC thermogram. T_g obtain from the DSC thermogram are presented in **Table 4.1**.

Table 4.1 Glass transition temperature of DPNR and HDPNR

Sample	Degree of Hydrogenation (%)	T_g (°C)
DPNR	-	-65
HDPNR I	0	-64
HDPNR II	6	-64
HDPNR III	7	-64
HDPNR IV	0	-65
HDPNR V	19	-63
HDPNR VI	34	-62
HDPNR VII	30	-62
HDPNR VIII	39	-61
HDPNR IX	75	-58
HDPNR X	34	-62
HDPNR XI	71	-59
HDPNR XII	70	-60
HDPNR XIII	0	-64
HDPNR XIV	2	-64
HDPNR XV	71	-59
HDPNR XVI	7	-64
HDPNRXVII	23	-63
HDPNR XVIII	52	-60
EPDM I[a]	-	-41
EPDM II[b]	-	-44
EPDM III	-	-49

[a] The ethylene-propylene copolymer (EPDM) has the ratio of ethylene/propylene as 67/33 and 4.3% of diene content.

[b] The EPDM has the ratio of ethylene/propylene as 53/47 and 6% of diene content.

[c] The EPDM has the ratio of ethylene/propylene as 52/48 and 8% of diene content.

The T_g value of DPNR, -65°C, demonstrate the rubber properties at room temperature and the glass properties below T_g. The Tg of HDPNR was slightly increased with an increase in the level of hydrogenation. The EPDM rubbers, having the higher Tg value of -41, -44 and -49°C, respectively, exhibits a higher degree of crystallization in the polymer structure than that of DPNR. Thus, it can be concluded that the hydrogenation reaction does not appreciably affect Tg of DPNR. Consequently, the hydrogenated rubber product still has a high rubbery property. A similar observation was also made by Singha and coworkers for hydrogenated NR obtained using the $RhCl(PPh_3)_3$ catalytic hydrogenation system [189].

4.1.3.2 Thermogravimetric Analysis (TGA)

Table 4.2 TGA results of DPNR and HDPNR

Sample	Degree of Hydrogenation (%)	T_{max} (°C)
DPNR	-	395
HDPNR I	0	395
HDPNR II	6	395
HDPNR III	7	395
HDPNR IV	0	395
HDPNR V	19	465
HDPNR VI	34	470
HDPNR VII	30	470
HDPNR VIII	39	471
HDPNR IX	75	475
HDPNR X	34	470
HDPNR XI	71	475
HDPNR XII	70	474
HDPNR XIII	0	395
HDPNR XIV	2	395
HDPNR XV	71	475
HDPNR XVI	7	395
HDPNRXVII	23	466
HDPNR XVIII	52	472
EPDM I[a]	-	492
EPDM II[b]	-	485
EPDM III	-	485

[a] The ethylene-propylene copolymer (EPDM) has the ratio of ethylene/propylene as 67/33 and 4.3% of diene content.

[b] The EPDM has the ratio of ethylene/propylene as 53/47 and 6% of diene content.

[c] The EPDM has the ratio of ethylene/propylene as 52/48 and 8% of diene content.

The degradation temperature (T_{max}) was calculated from the peak maximum of the derivative of the TGA curves. The T_{max} values from TGA measurement of HDPNR are shown in **Table 4.2**. The results suggest that T_{max} increased with increasing reduction of carbon-carbon double bonds in DPNR. This can be explained, in that the C=C bonds in DPNR consist of a strong σ bond and a weak π bond and the hydrogenation reaction involves the breakage of a weak π bond by the hydrogen molecule to from C-H σ bond, which leads to the higher thermal stability. In comparison with those of EPDM rubbers, the degradation temperature of HDPNR was very closed those of EPDM rubbers. It can be concluded that HDPNR provide a facile entry to alternating EPDMs.

For another reason, because of the HDPNR is the partial hydrogenated product of DPNR, therefore the residual unsaturated units that are located in a random manner in the molecular chain might be degraded in the first place, while the rigid part obtained after hydrogenation can resist the high temperature applied for a longer time.

CHAPTER V

CONCLUSIONS

The homogeneous catalytic hydrogenation process of DPNR using Palladium (II) acetate ($Pd(OAc)_2$) as a catalyst and the various parameters influenced on HDPNR preparation were concluded as following.

First, for HDPNR preparation from hydrogenation technique, the microstructure of HDPNR and thermal behaviors of HDPNR, respectively, it was found that The FTIR spectra of DPNR showed the absorbance at 735 cm^{-1} and the intensity of the peaks at 1,665 and 836 cm^{-1} were gradually decreased after hydrogenation process. ^1H-NMR showed the appearance of the signal at 0.8 and 1.2 ppm, which are yhe protons of saturated unit. The additional signals at 19.69, 24.44, 32.74 and 37.37 ppm were detected in the HDPNR sample. These signals correspond to the carbon of saturated unit were determined by ^{13}C-NMR. Thermal behavior of hydrogenated rubbers can be characterized by DSC and TGA. The DSC thermogram showed that the T_g values of HDPNR were slightly higher than DPNR and the TGA data showed T_{max} value increased with increasing reduction of carbon-carbon double bonds in DPNR Thus, it can be concluded that the hydrogenation reaction does not appreciably affect T_g of DPNR and it is high potential to prepare hydrogenated NR in the latex state.

Finally, based on the study of some effects on hydrogenation reaction, it could be concluded that the optimum condition was achieved from ratio (catalyst/rubber) 0.0600 under 3 MPa H_2 pressure at 50°C for 6 h.

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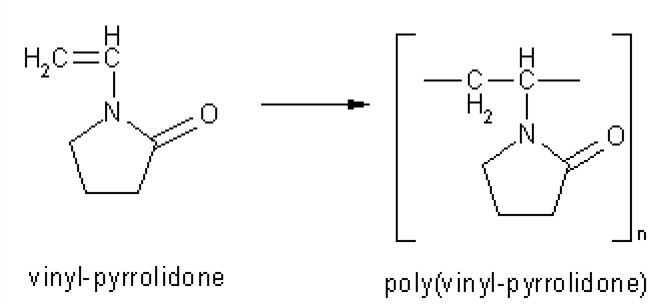
APPENDIX

Appendix A Polyvinyl pyrrolidone (PVP)



Properties

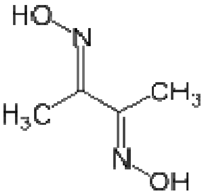
PVP is soluble in water and other polar solvents. In water it has the useful property of Newtonian viscosity. When dry it is a light flaky powder, which readily absorbs up to 18% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. The monomer is carcinogenic and is extremely toxic to aquatic life. However the polymer PVP in its pure form is so safe that not only is it edible by humans, it was used as a blood plasma expander for trauma victims after the first half of 20th century.

It is used as a binder in many pharmaceutical tablets; being completely inert to humans, it simply passes through. PVP added to Iodine forms a complex; in solution it is known under the trade name Betadine.

PVP binds to polar molecules exceptionally well, owing to its polarity. This has led to its application in coatings for photo-quality ink-jet papers and transparencies, as well as in inks for inkjet printers.

PVP is also used in personal care products, such as shampoos and toothpastes, in paints, and adhesives that you have to moisten, such as old-style postage stamps and envelopes. It has also been used in contact lens solutions and in steel-quenching solutions. PVP is the basis of the early formulas for hair sprays and hair gels, and still continues to be a component of some.

Appendix B Dimethylglyoxime (DMG)



Dimethylglyoxime is a chemical compound described by the formula $CH_3C(NOH)C(NOH)CH_3$. It is the dioxime derivative of the diketone diacetyl (also known as 2,3-butanedione). $DmgH_2$ is used in the analysis of palladium or nickel. Its coordination complexes are of theoretical interest as models for enzymes and as catalysts. Many related ligands can be prepared from other diketones, e.g. benzil. Although commercially available, dimethylglyoxime can be prepared by the reaction of diacetyl and hydroxylamine:

$$CH_3C(O)C(O)CH_3 + 2\ NH_2OH \rightarrow CH_3C(NOH)C(NOH)CH_3 + 2\ H_2O$$

$Ni(dmgH)_2$

As an analytical reagent, dmgH2 is often used as a solution in ethanol. It is the conjugate base, not $dmgH_2$ itself, that forms the complexes. Furthermore, a pair of $dmgH^-$ ligands are joined through hydrogen bonds to give a macrocyclic ligand. The most famous complex is the bright red $Ni(dmgH)_2$, formed by treatment of Ni(II) sources with $dmgH_2$. This planar complex is very poorly soluble and is used for the gravimetric determination of nickel, e.g. in ores.

Appendix C. Differential Scanning Calorimetry (DSC)

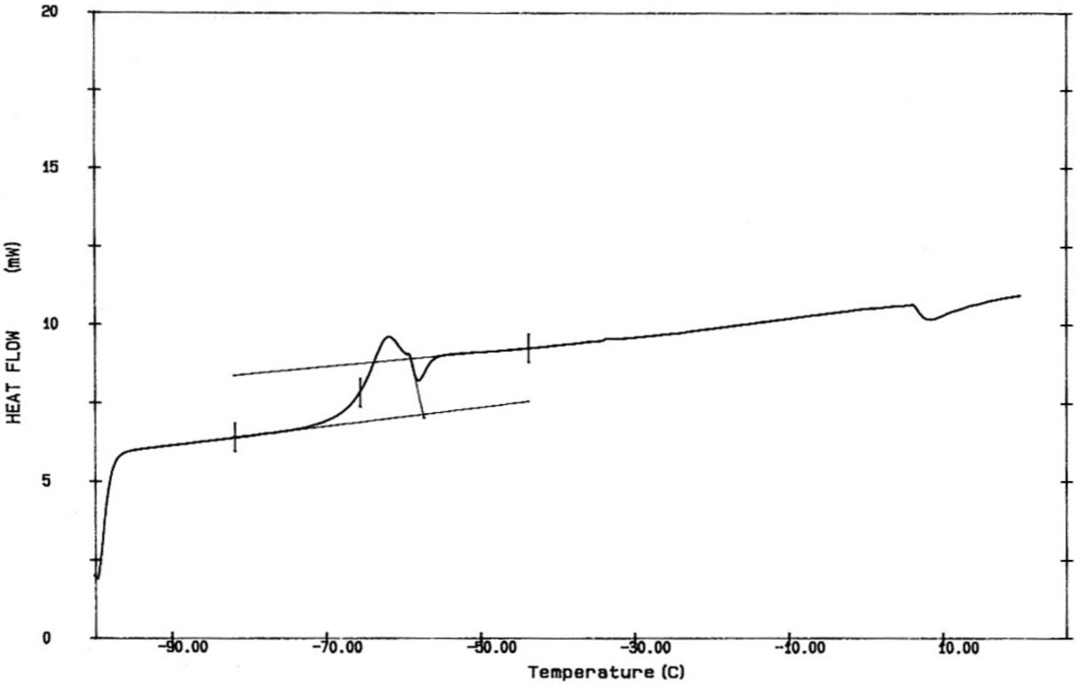


Figure C-1 DSC thermogram of DPNR

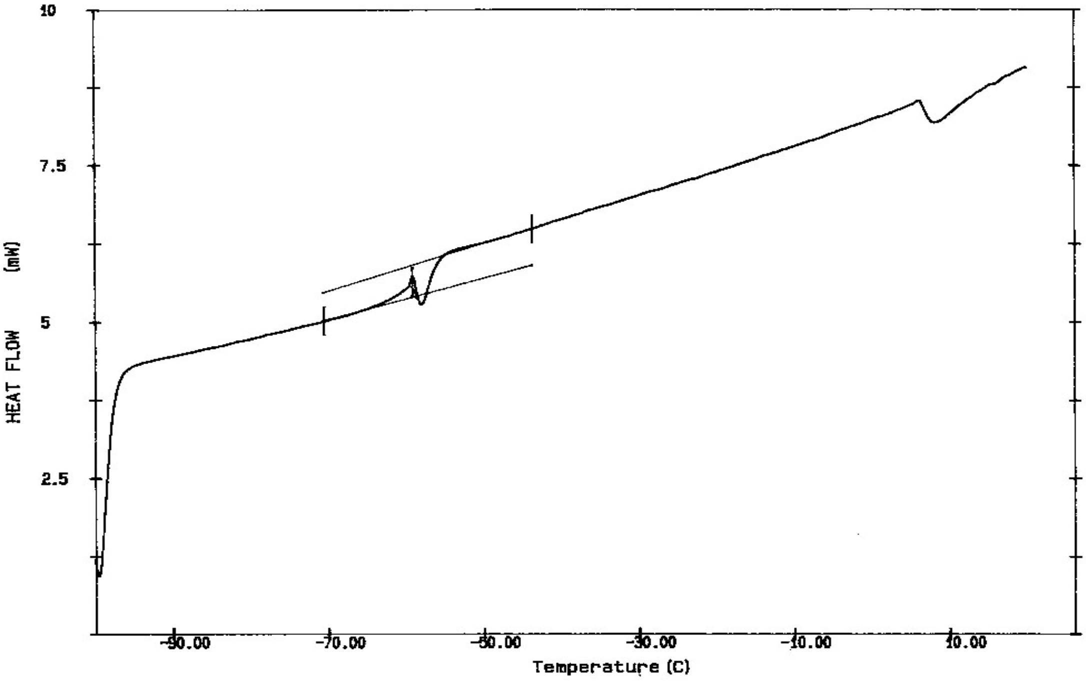


Figure C-2 DSC thermogram of HDPNR I

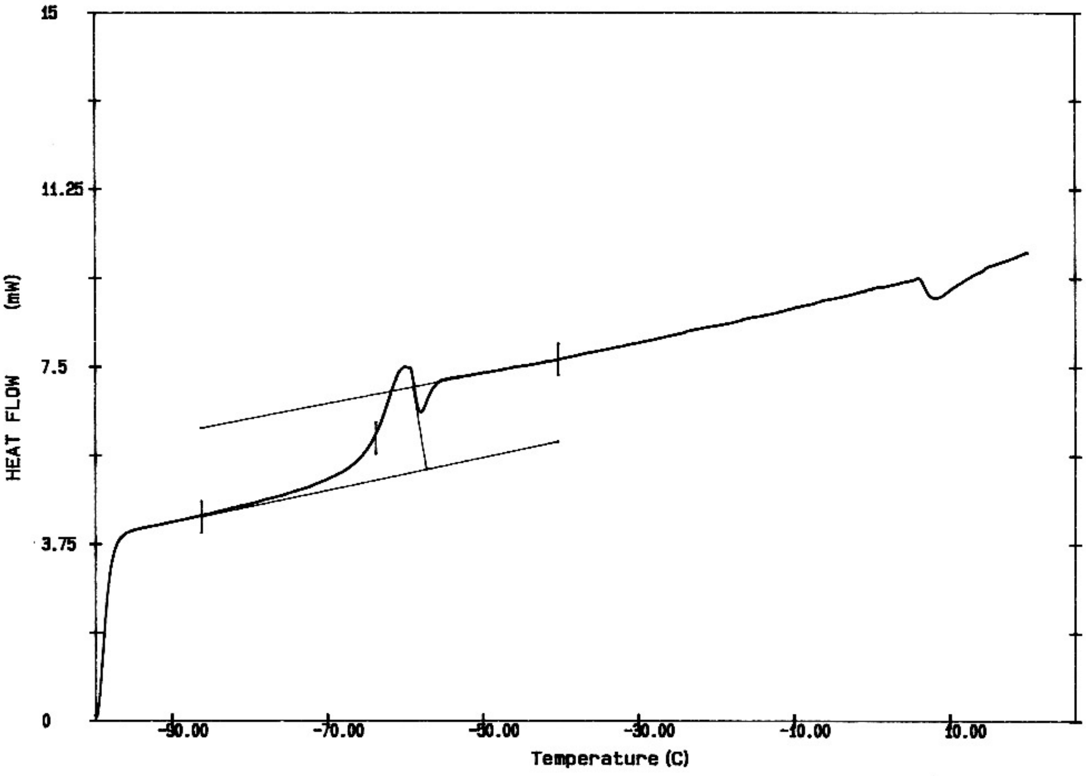


Figure C-3 DSC thermogram of HDPNR II

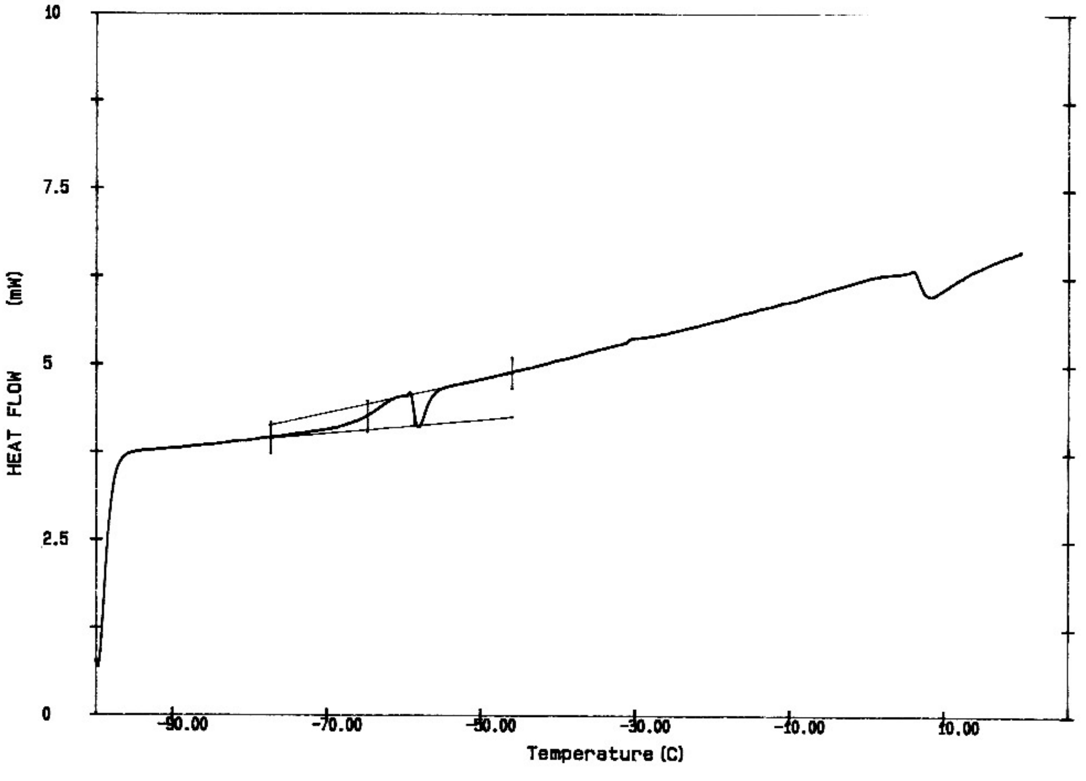


Figure C-4 DSC thermogram of HDPNR III

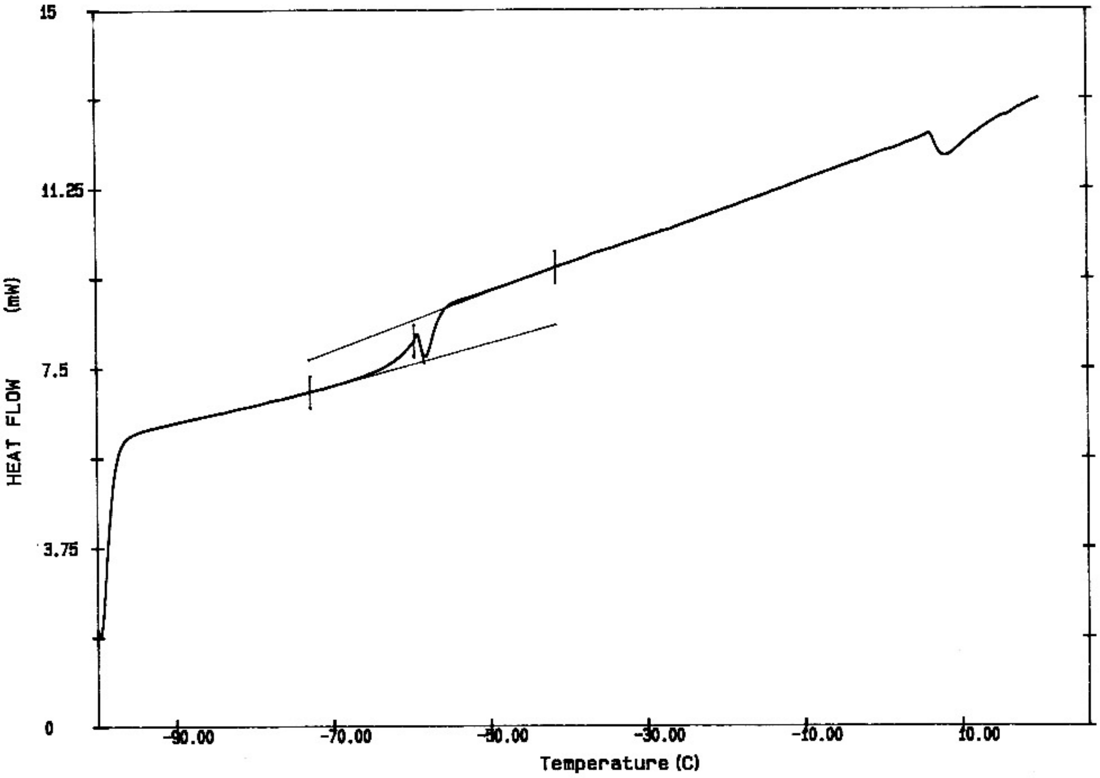


Figure C-5 DSC thermogram of HDPNR IV

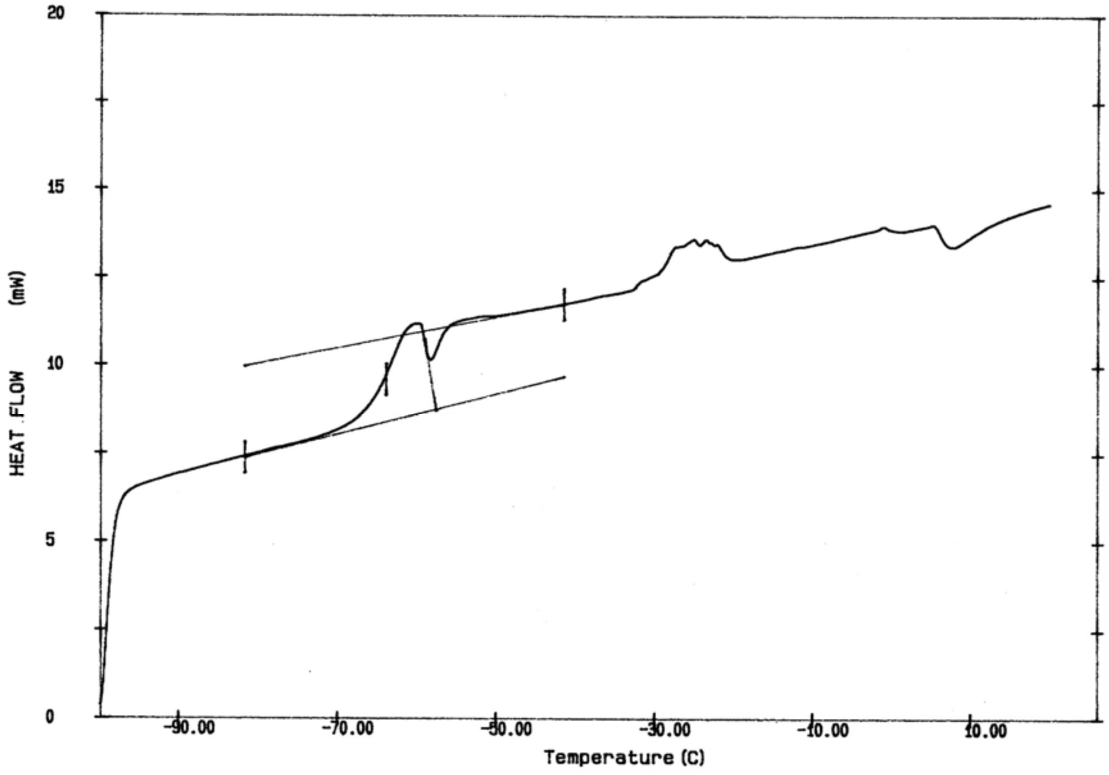


Figure C-6 DSC thermogram of HDPNR V

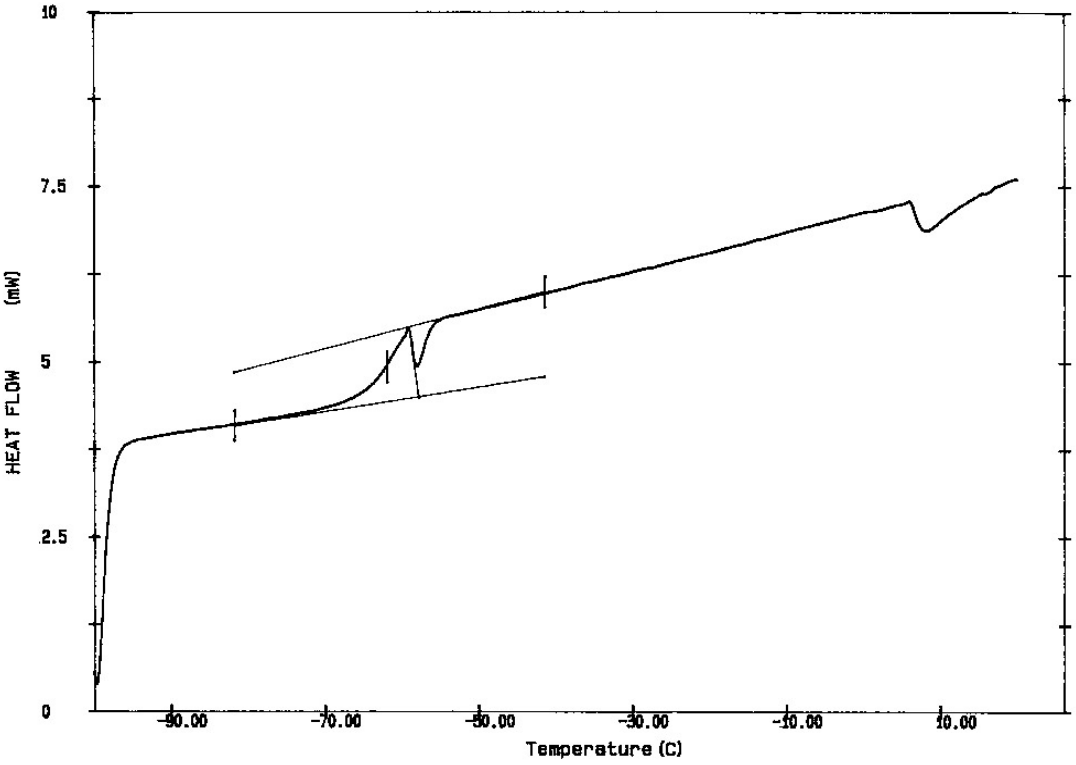


Figure C-7 DSC thermogram of HDPNR VI

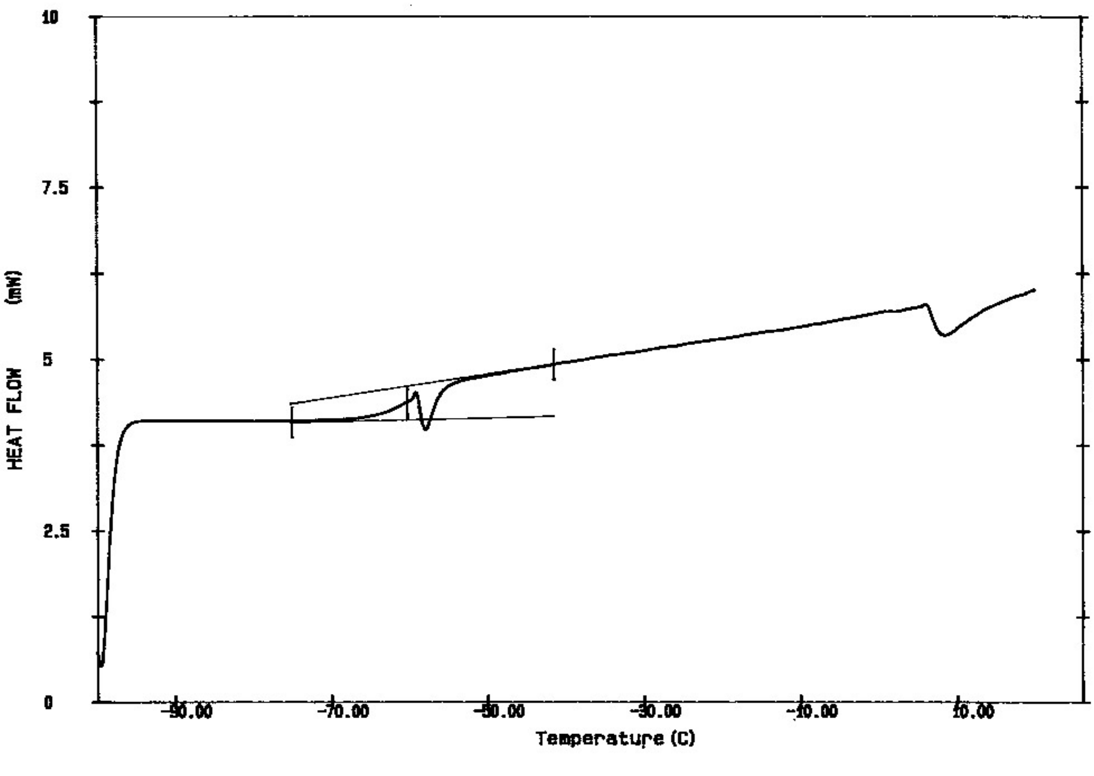


Figure C-8 DSC thermogram of HDPNR VII

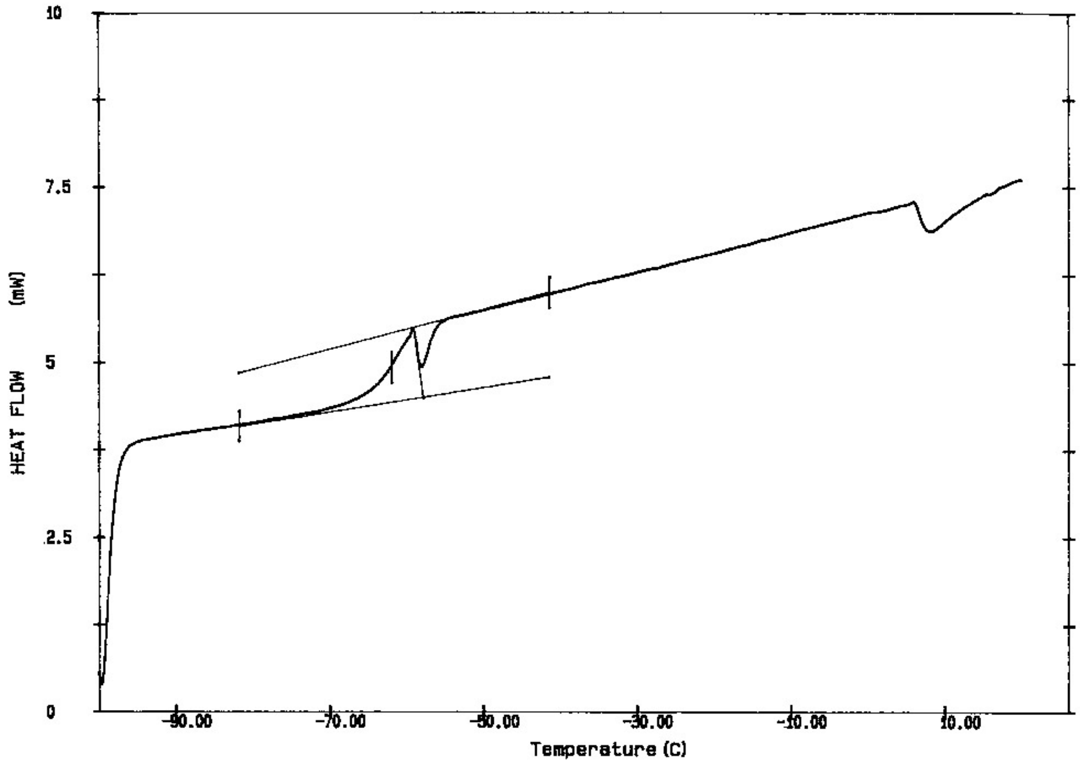


Figure C-9 DSC thermogram of HDPNR VIII

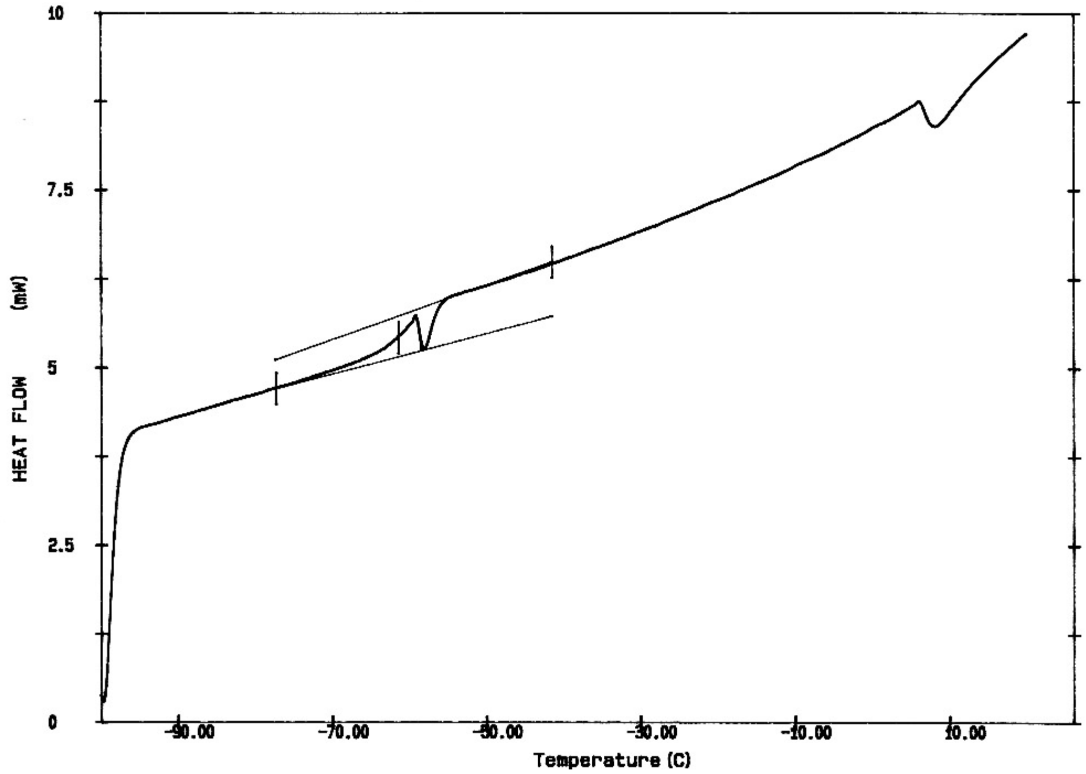


Figure C-10 DSC thermogram of HDPNR IX

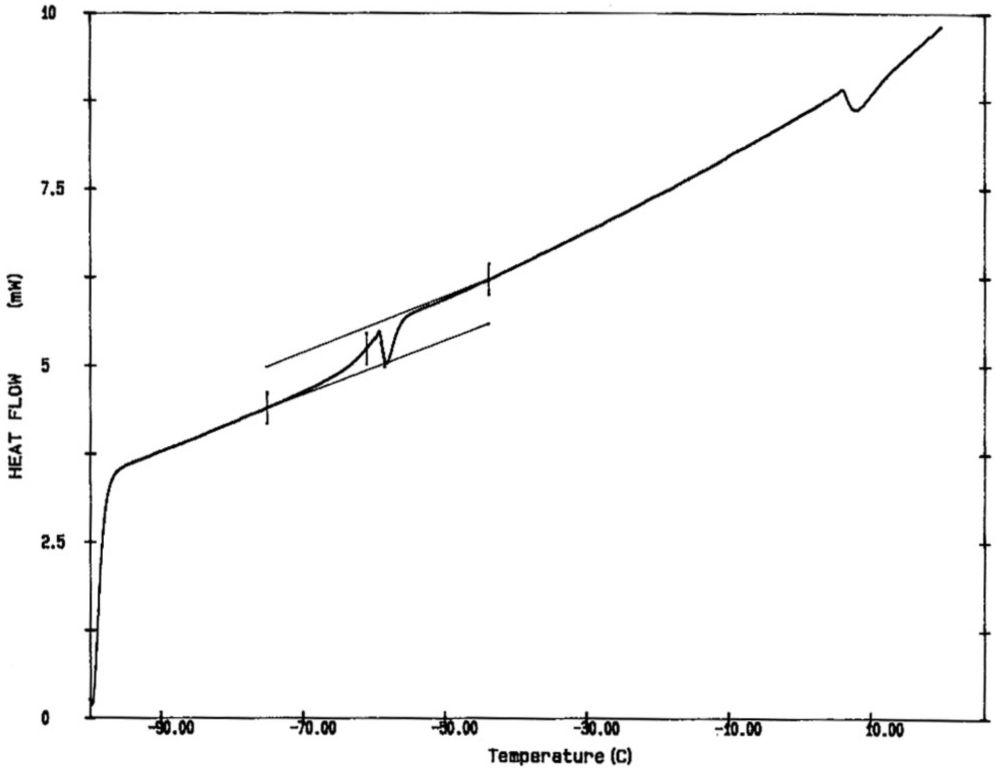


Figure C-11 DSC thermogram of HDPNR X

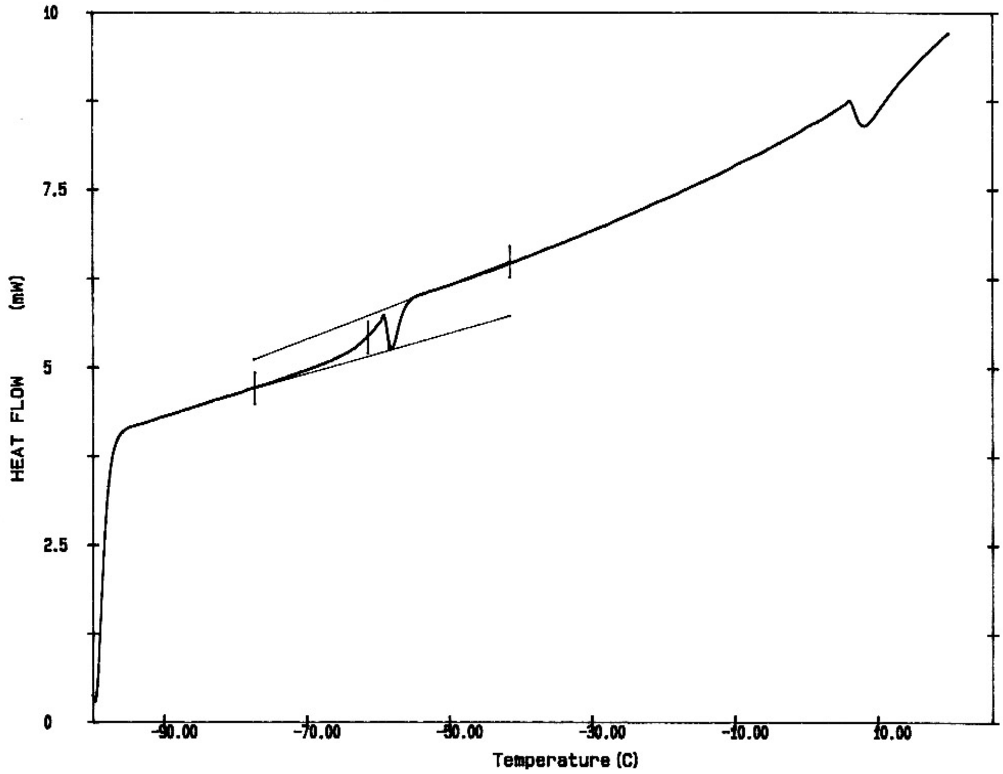


Figure C-12 DSC thermogram of HDPNR XI

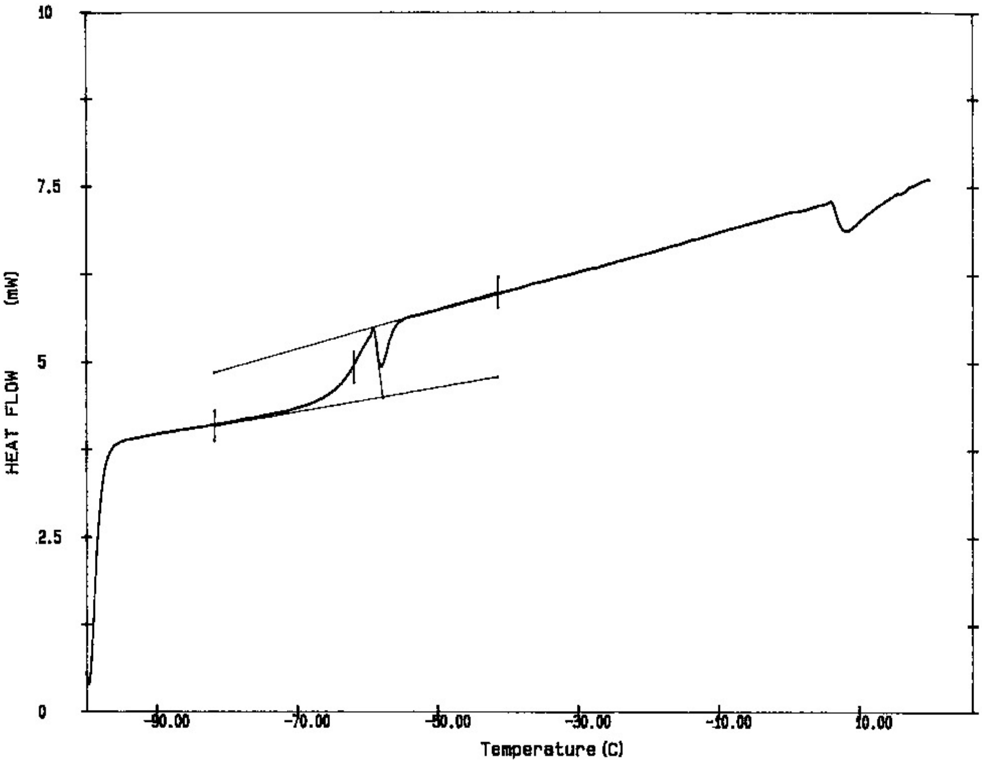


Figure C-13 DSC thermogram of HDPNR XII

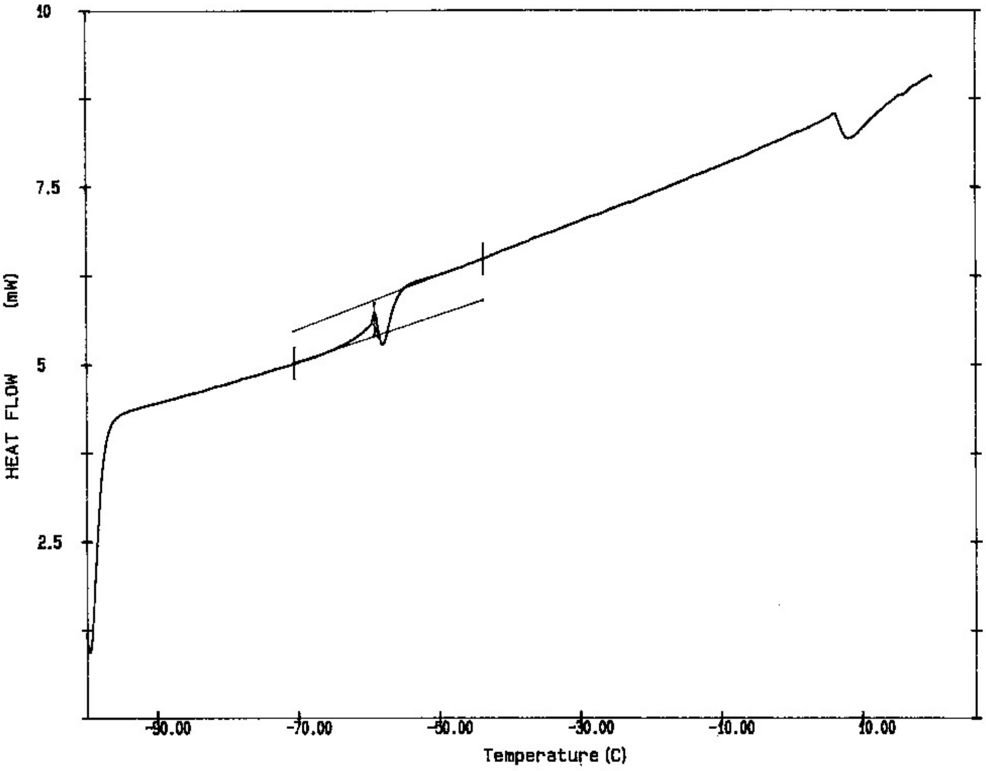


Figure C-14 DSC thermogram of HDPNR XIII

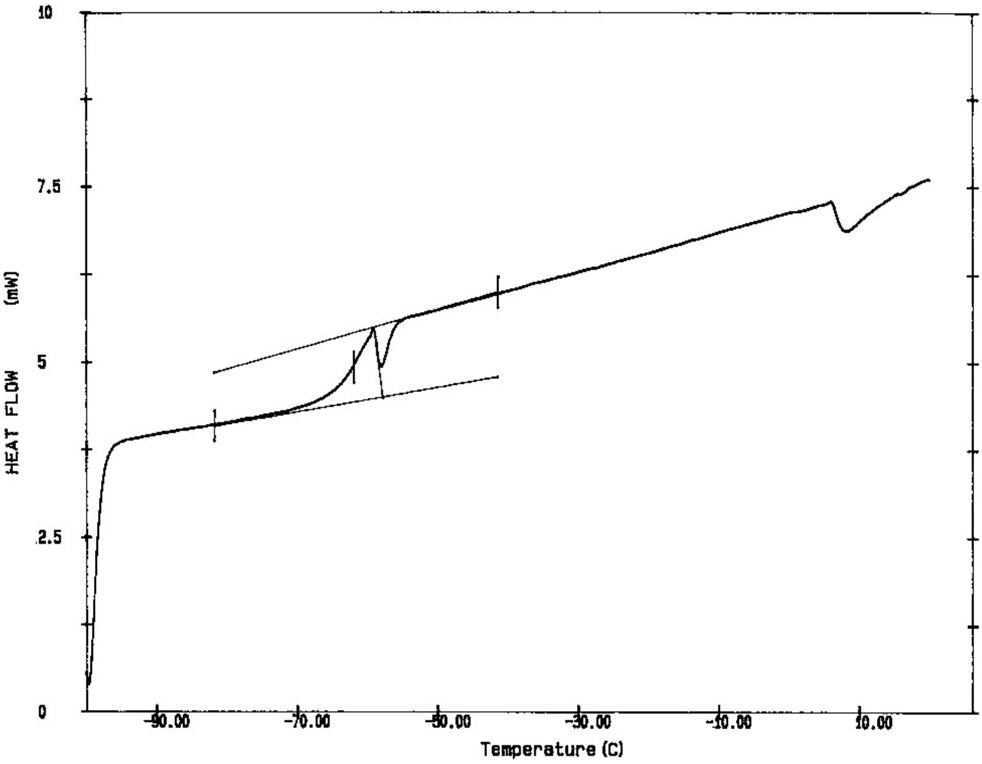


Figure C-15 DSC thermogram of HDPNR XIV

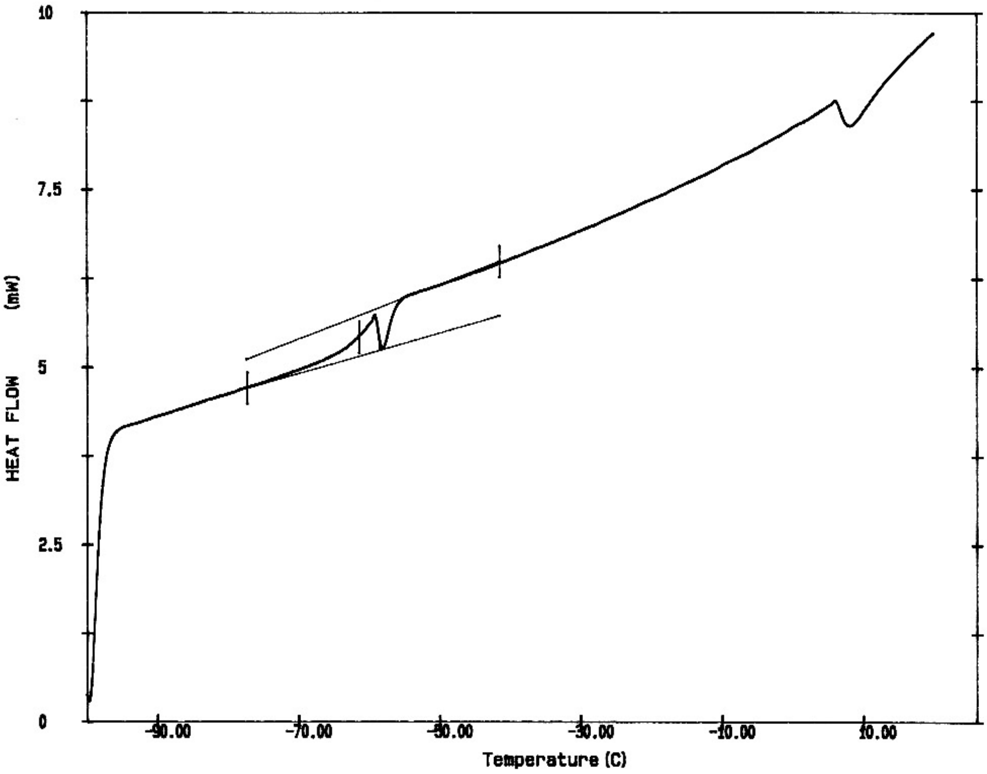


Figure C-16 DSC thermogram of HDPNR XV

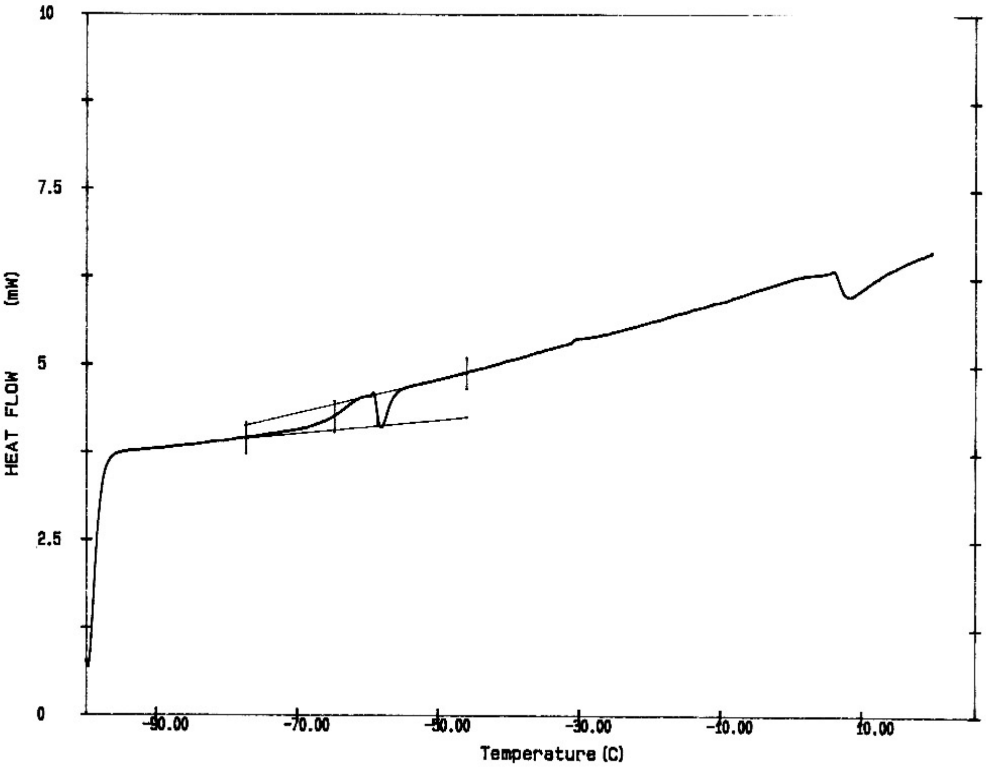


Figure C-17 DSC thermogram of HDPNR XVI

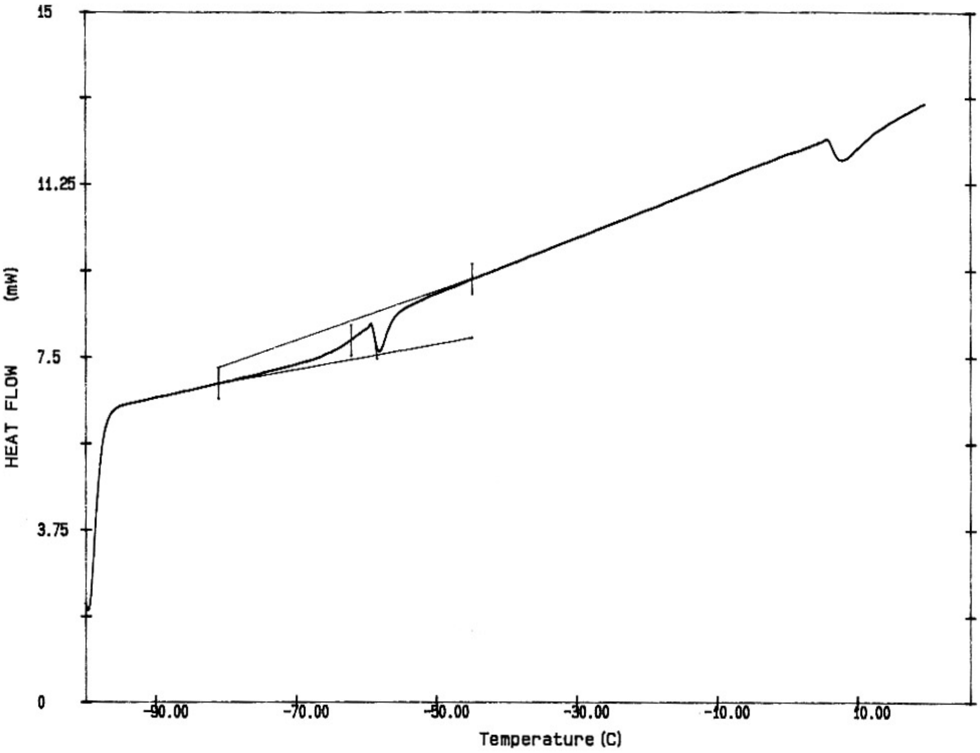


Figure C-18 DSC thermogram of HDPNR XVII

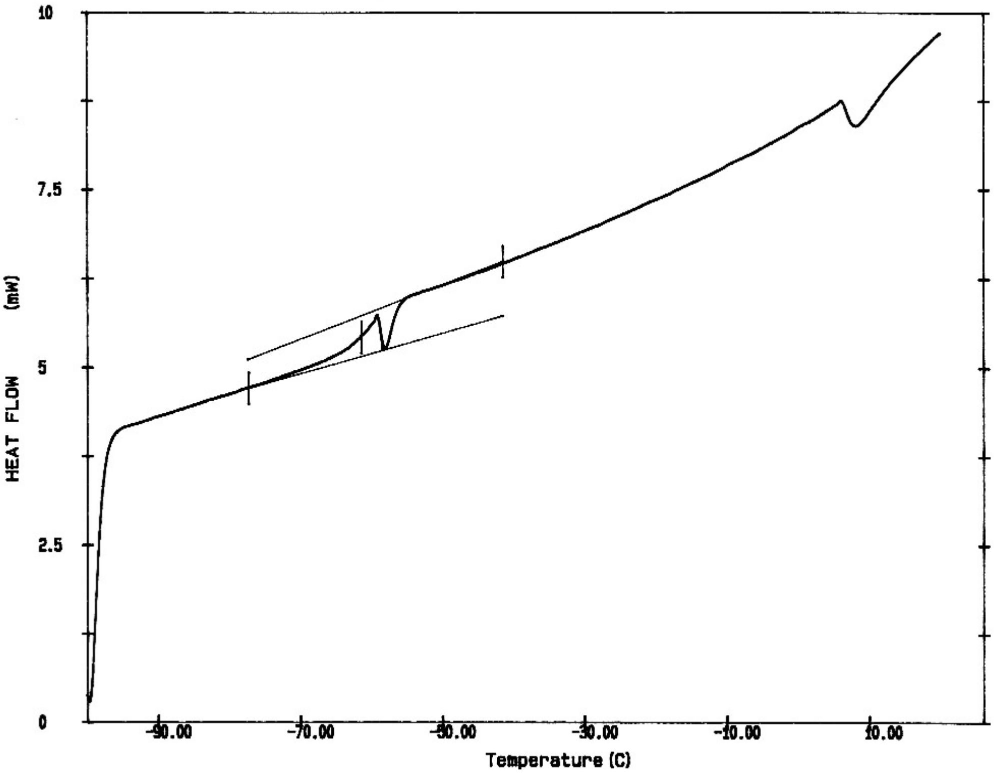


Figure C-19 DSC thermogram of HDPNR XVIII

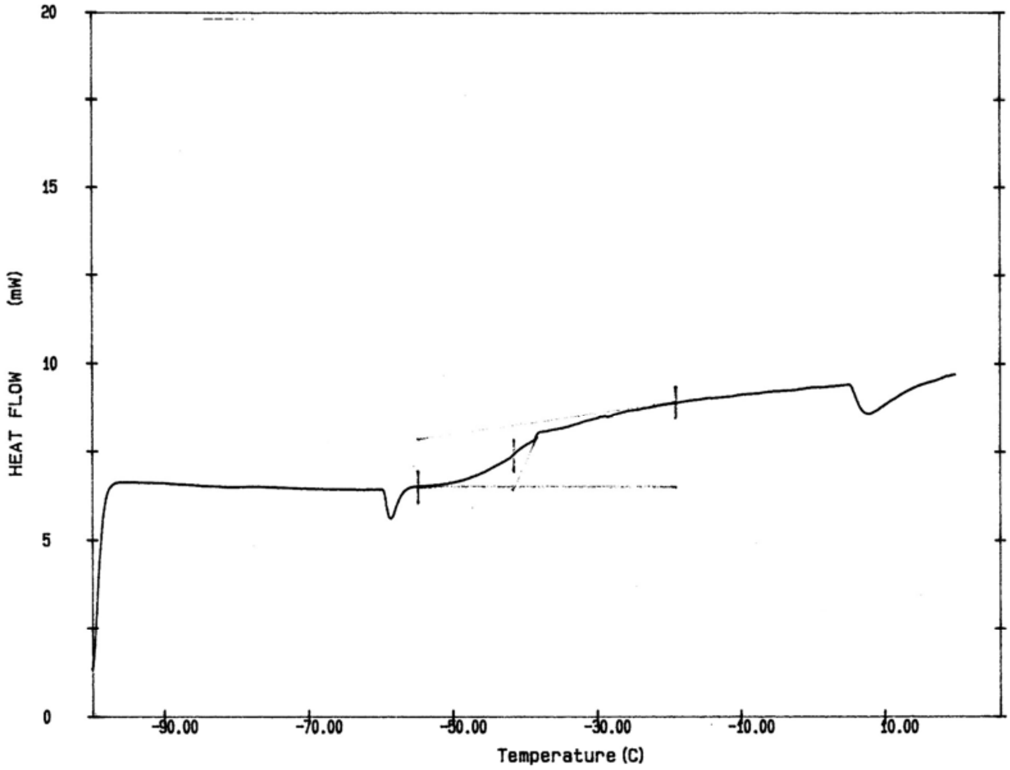


Figure C20 DSC thermogram of EPDM I

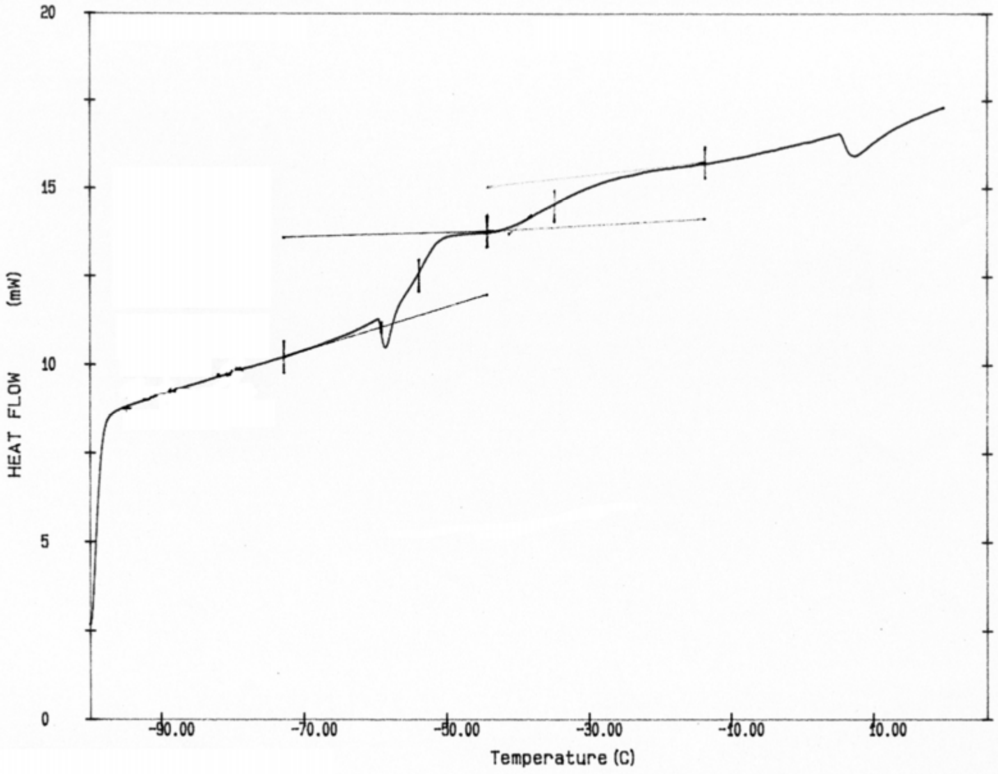


Figure C21 DSC thermogram of EPDM II

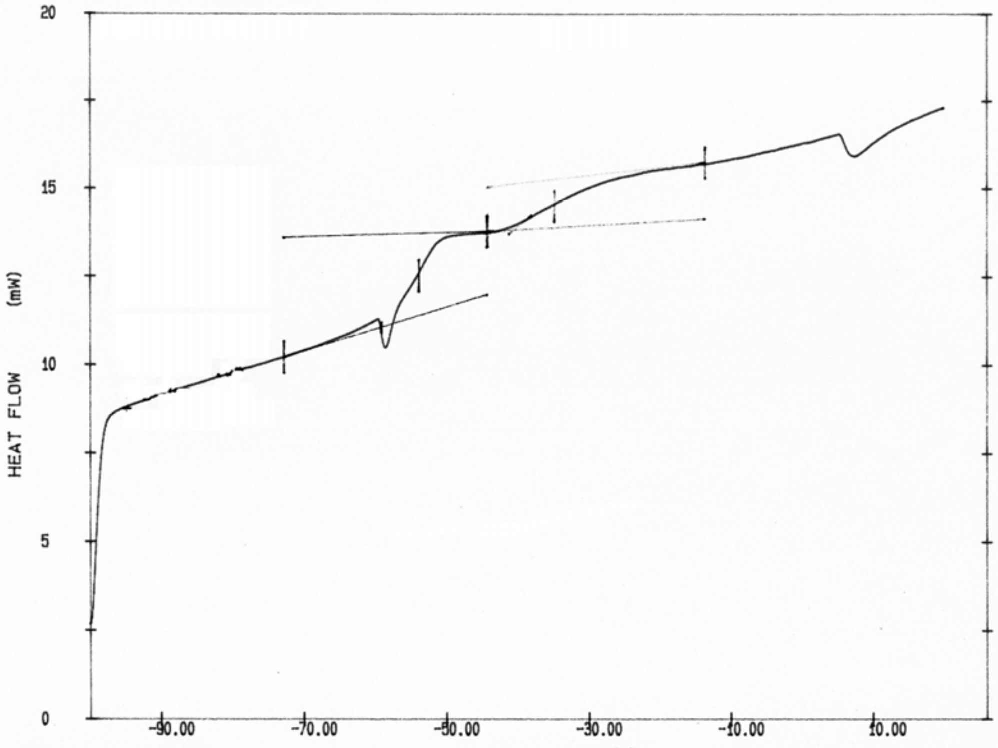


Figure C22 DSC thermogram of EPDM III

Appendix D Thermogravimetric Analysis (TGA)

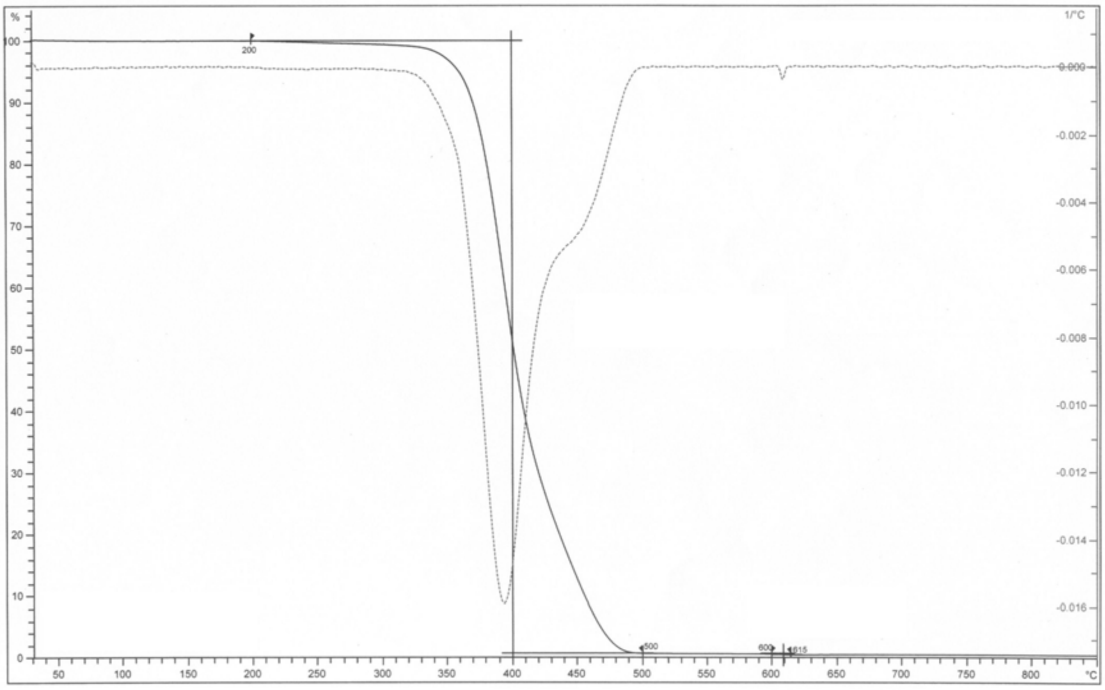


Figure D-1 TGA thermogram of DPNR

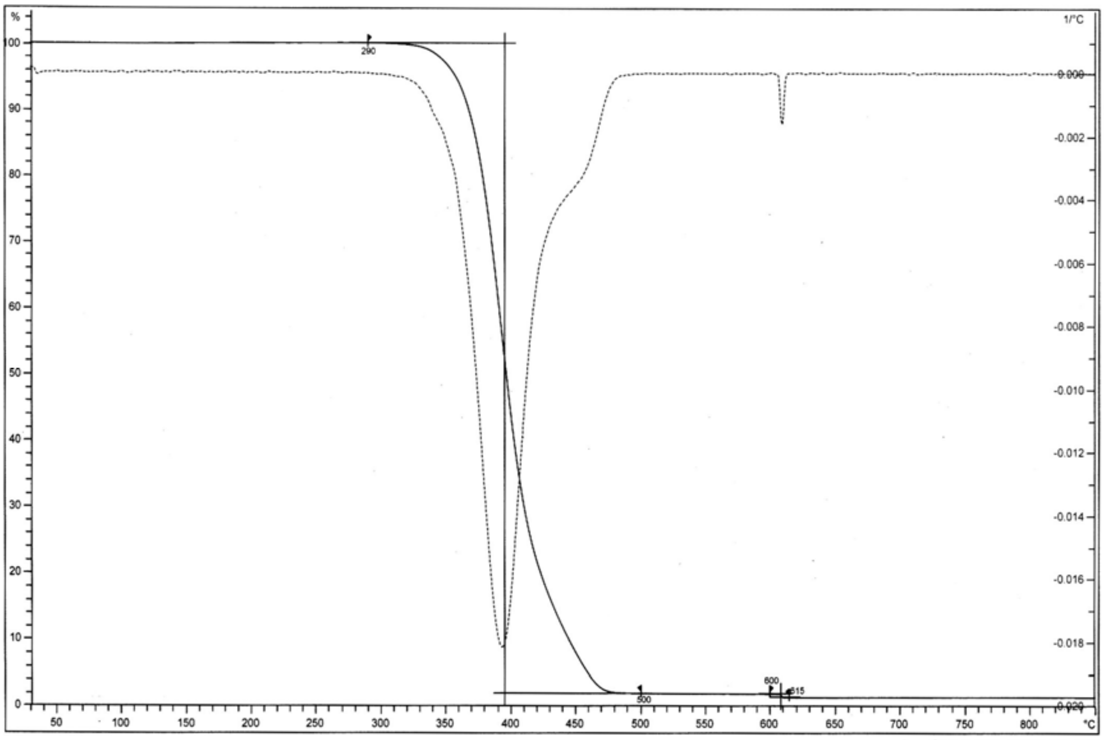


Figure D-2 TGA thermogram of HDPNR I

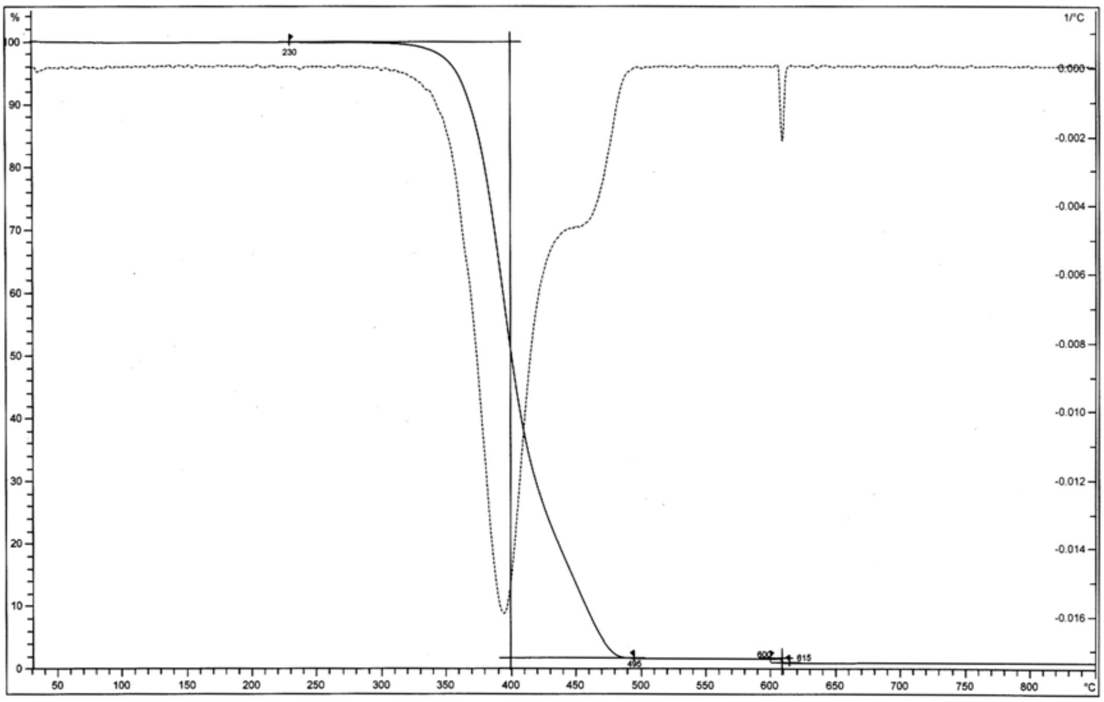


Figure D-3 TGA thermogram of HDPNR II

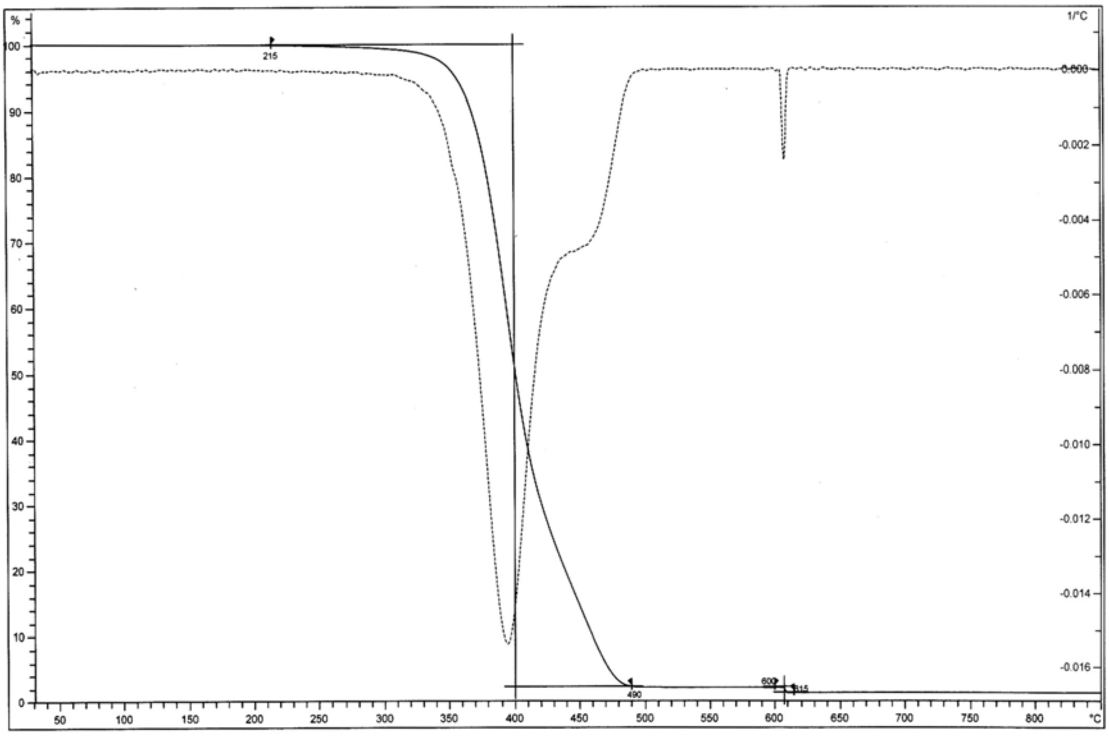


Figure D-4 TGA thermogram of HDPNR III

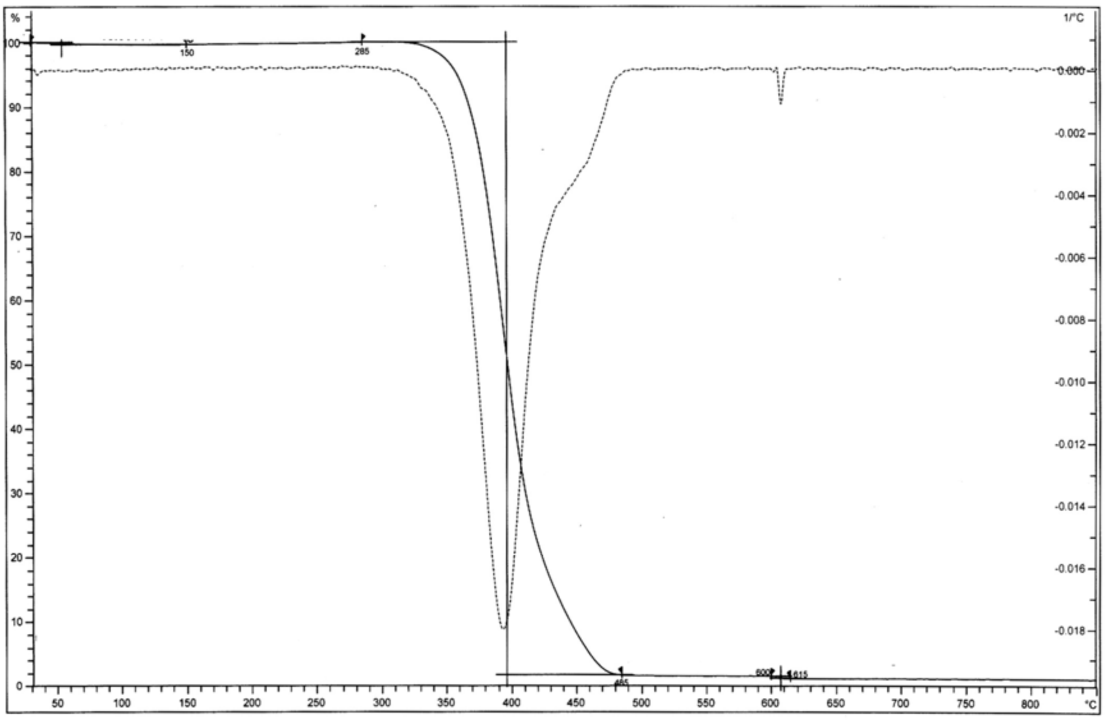


Figure D-5 TGA thermogram of HDPNR IV

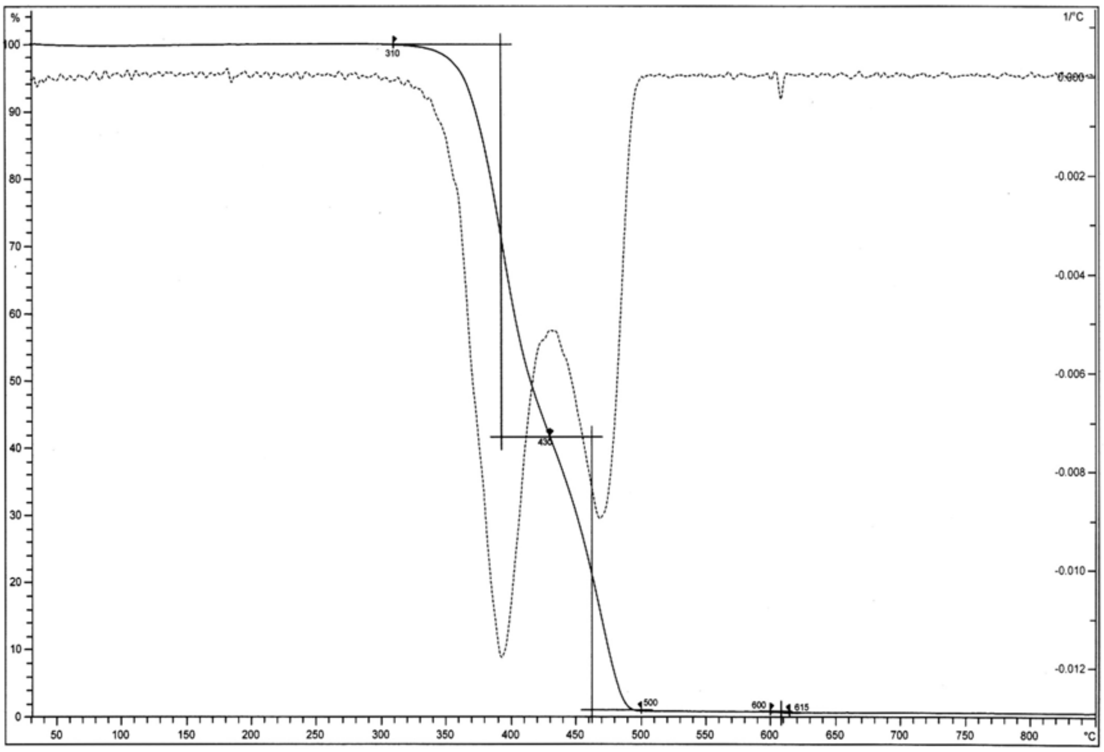


Figure D-6 TGA thermogram of HDPNR V

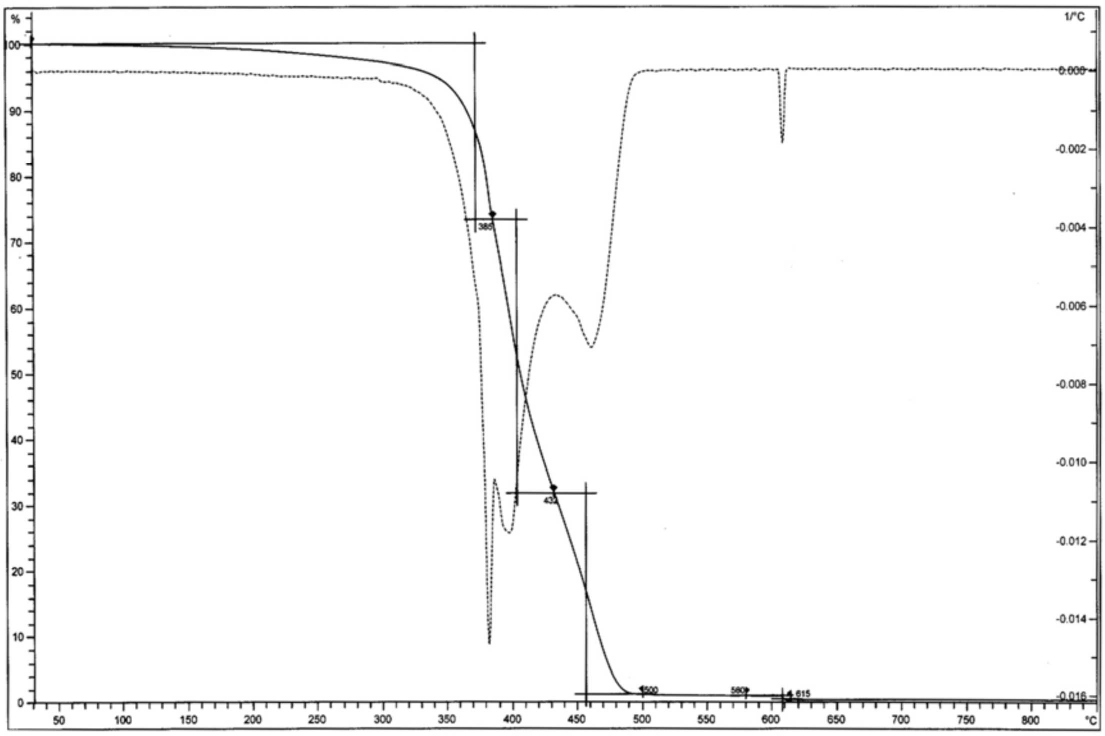


Figure D-7 TGA thermogram of HDPNR VI

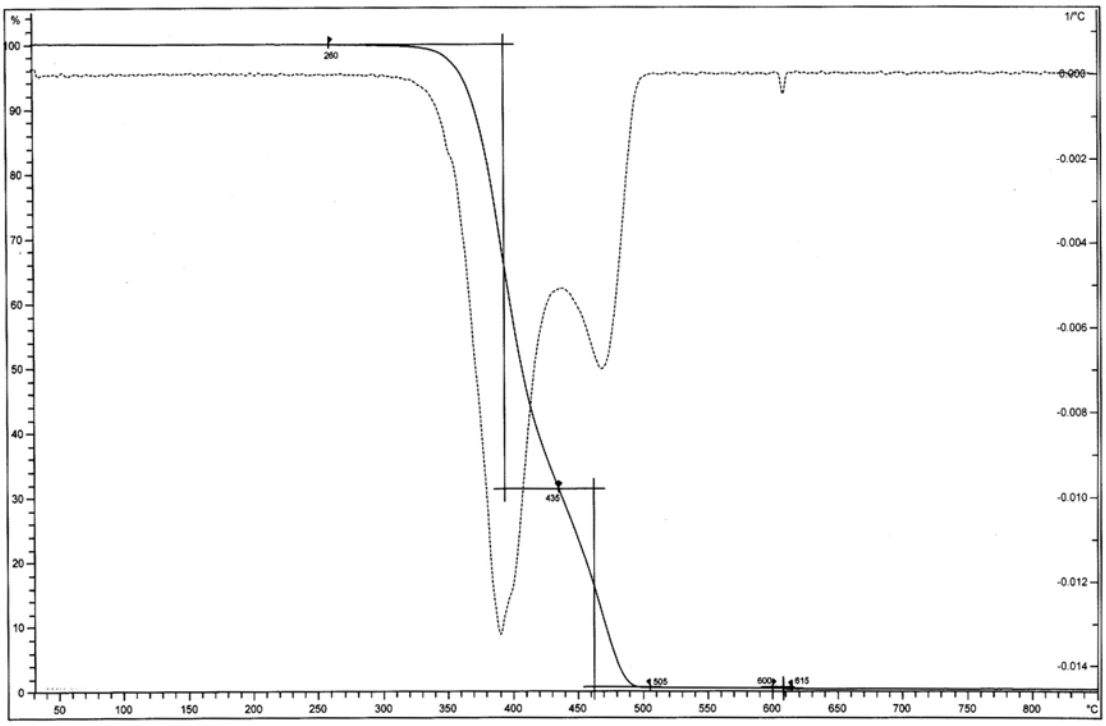


Figure D-8 TGA thermogram of HDPNR VII

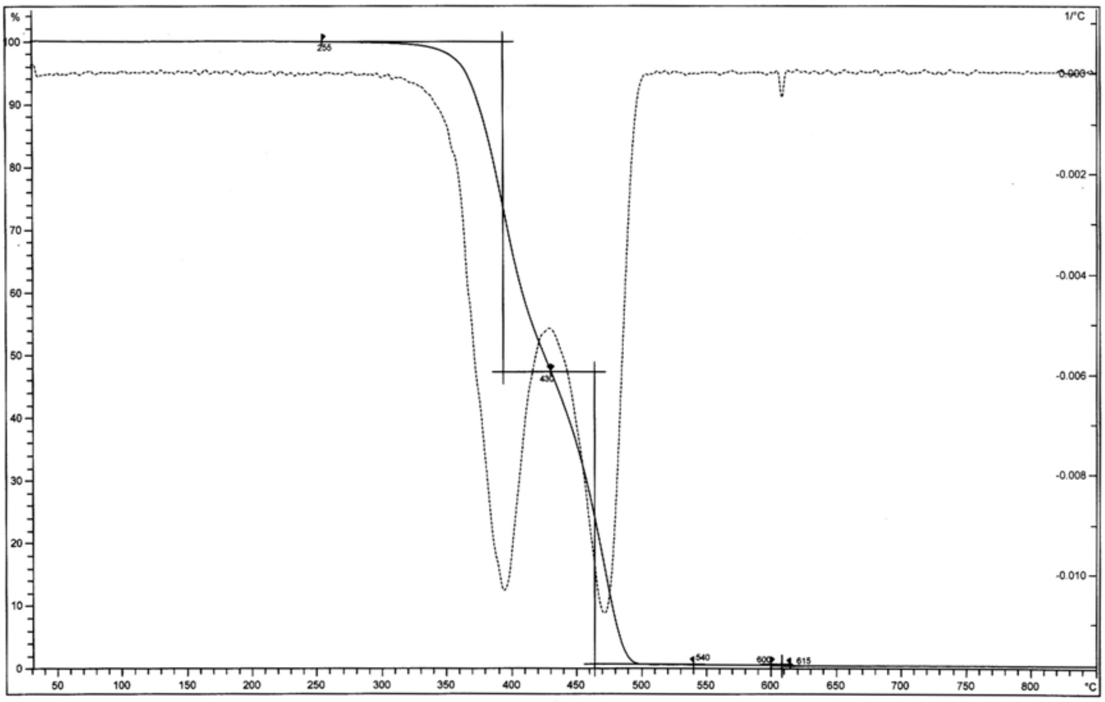


Figure D-9 TGA thermogram of HDPNR VIII

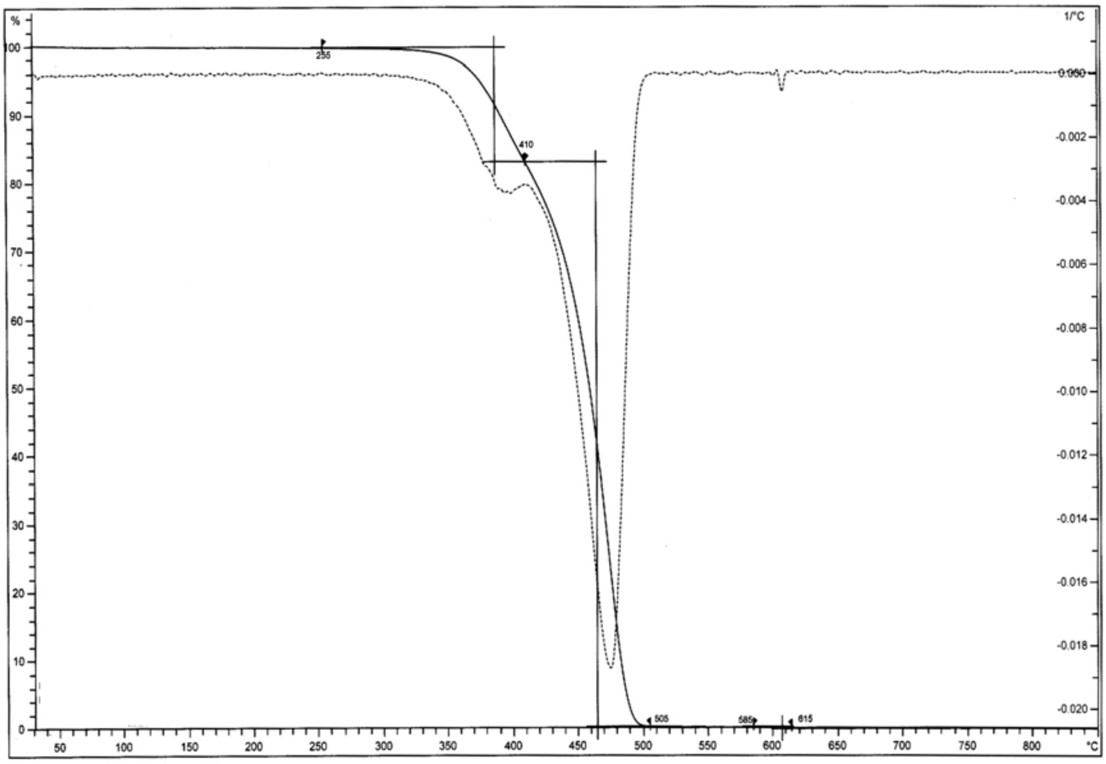


Figure D-10 TGA thermogram of HDPNR IX

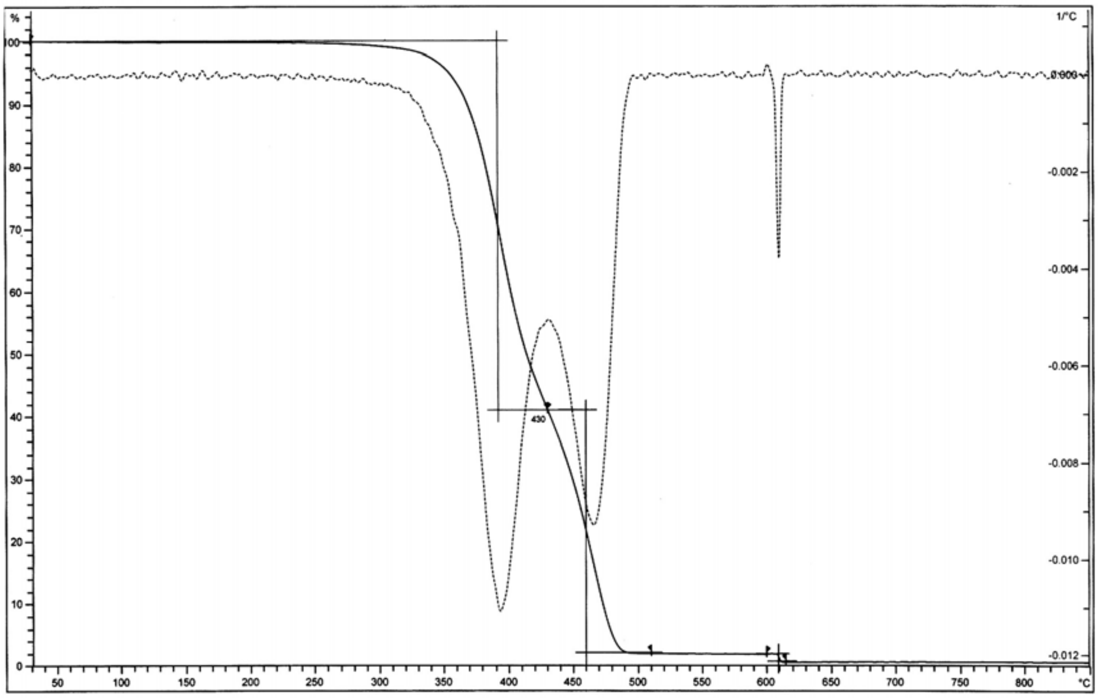


Figure D-11 TGA thermogram of HDPNR X

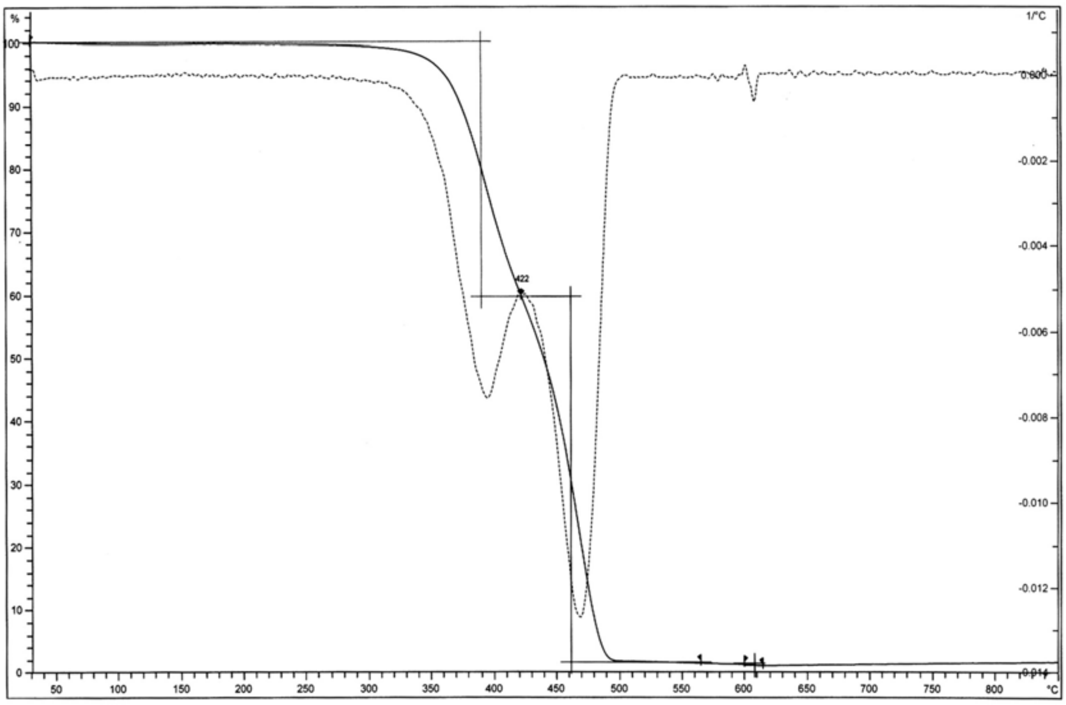


Figure D-12 TGA thermogram of HDPNR XI

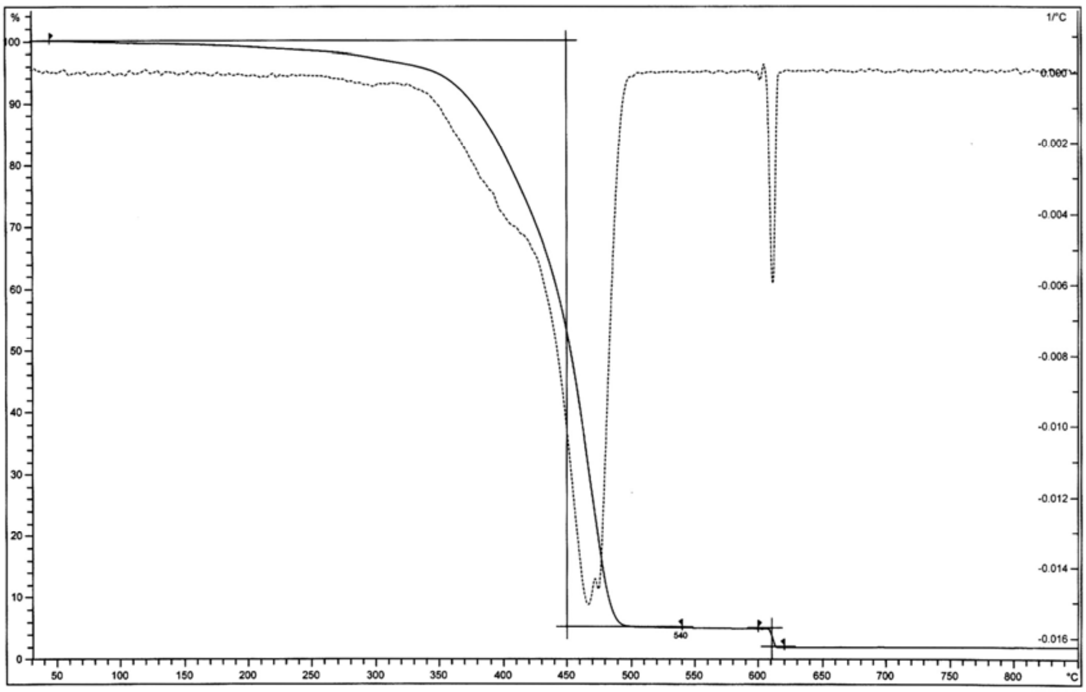


Figure D-13 TGA thermogram of HDPNR XII

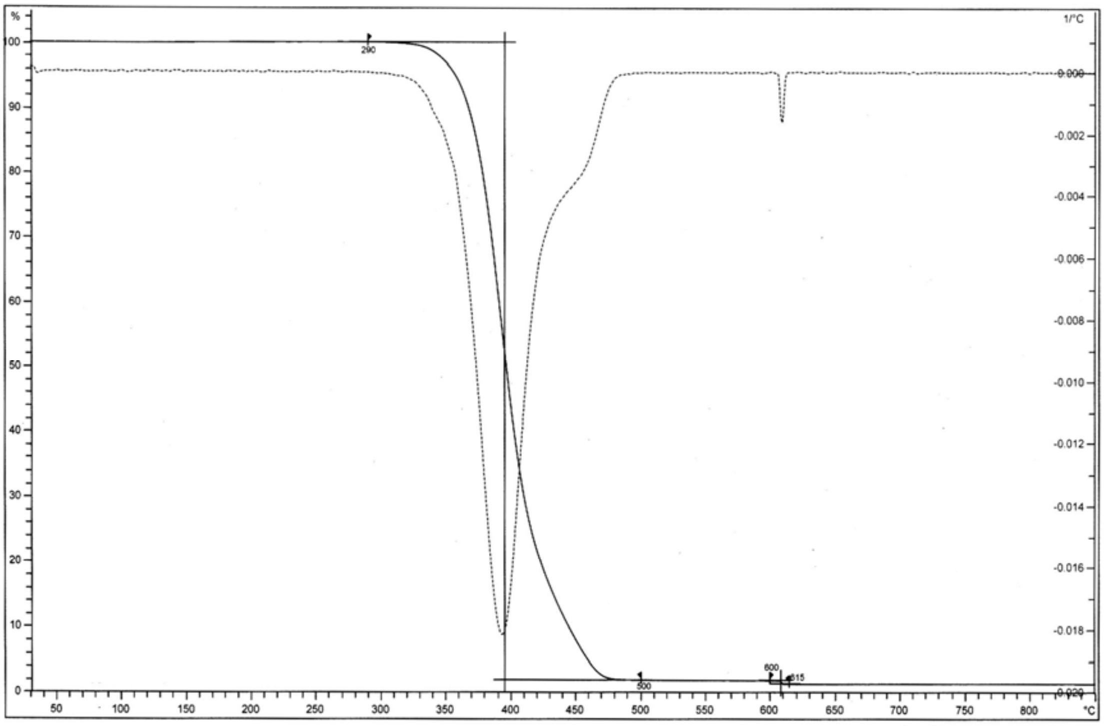


Figure D-14 TGA thermogram of HDPNR XIII

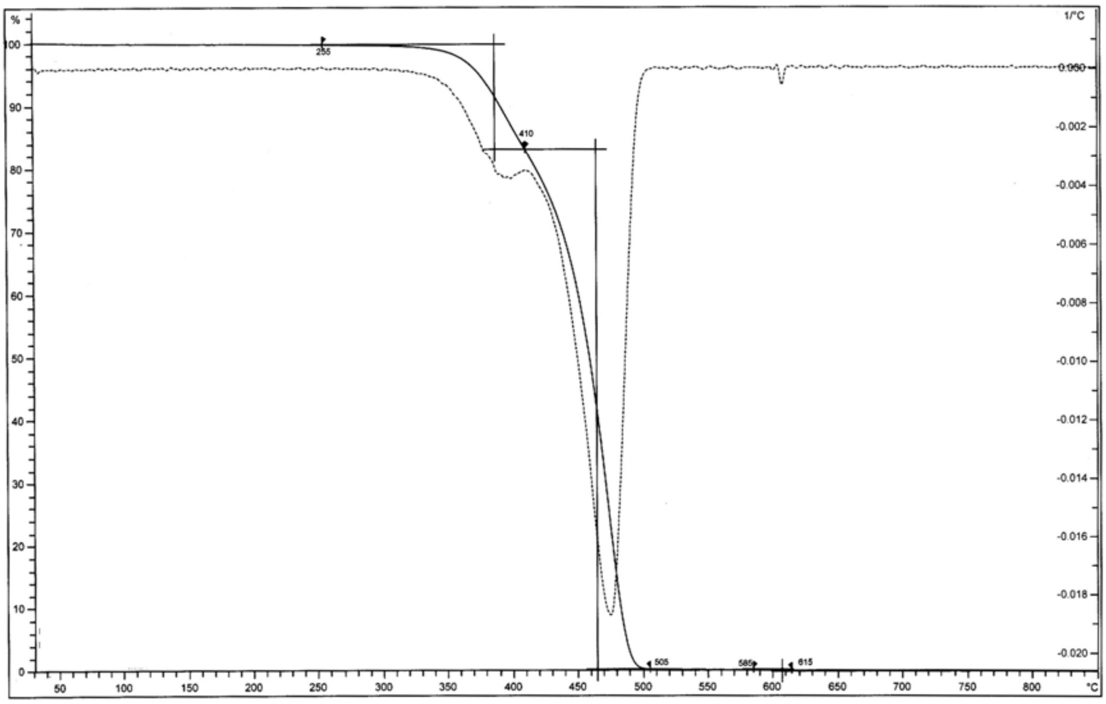


Figure D-15 TGA thermogram of HDPNR XIV

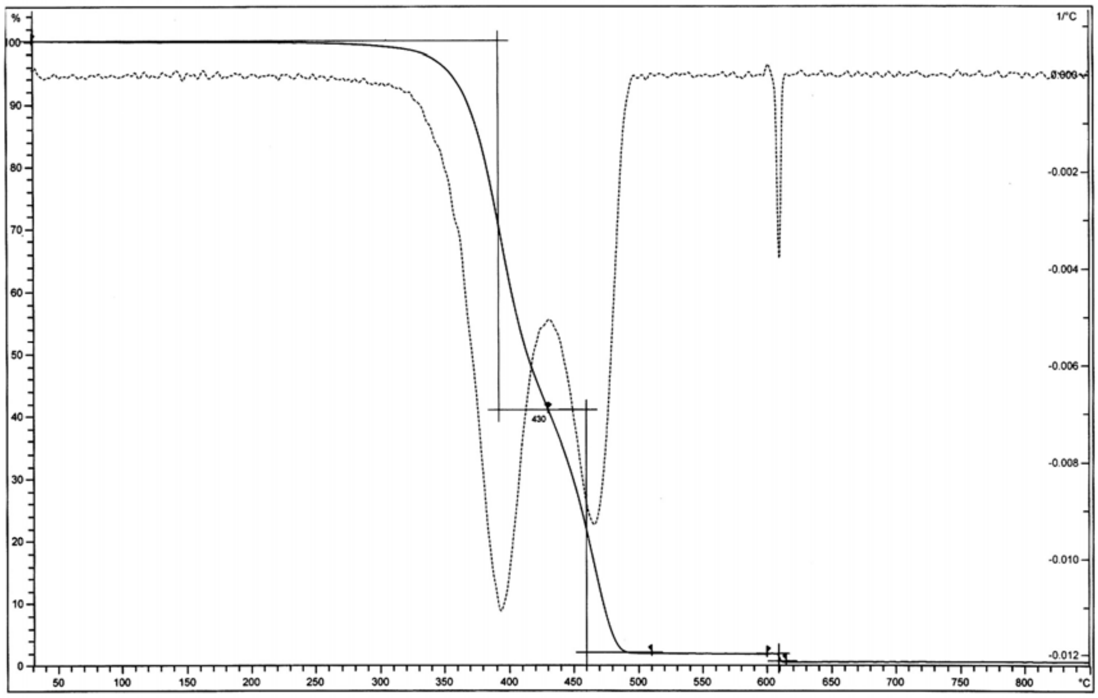


Figure D-16 TGA thermogram of HDPNR XV

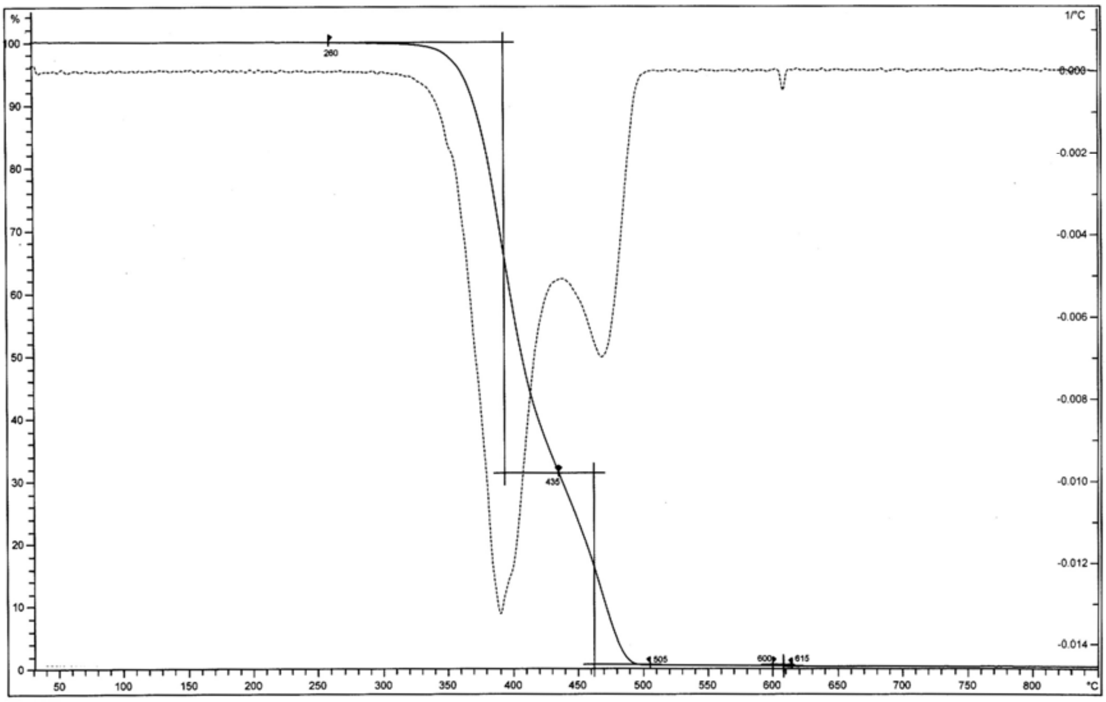


Figure D-17 TGA thermogram of HDPNR XVI

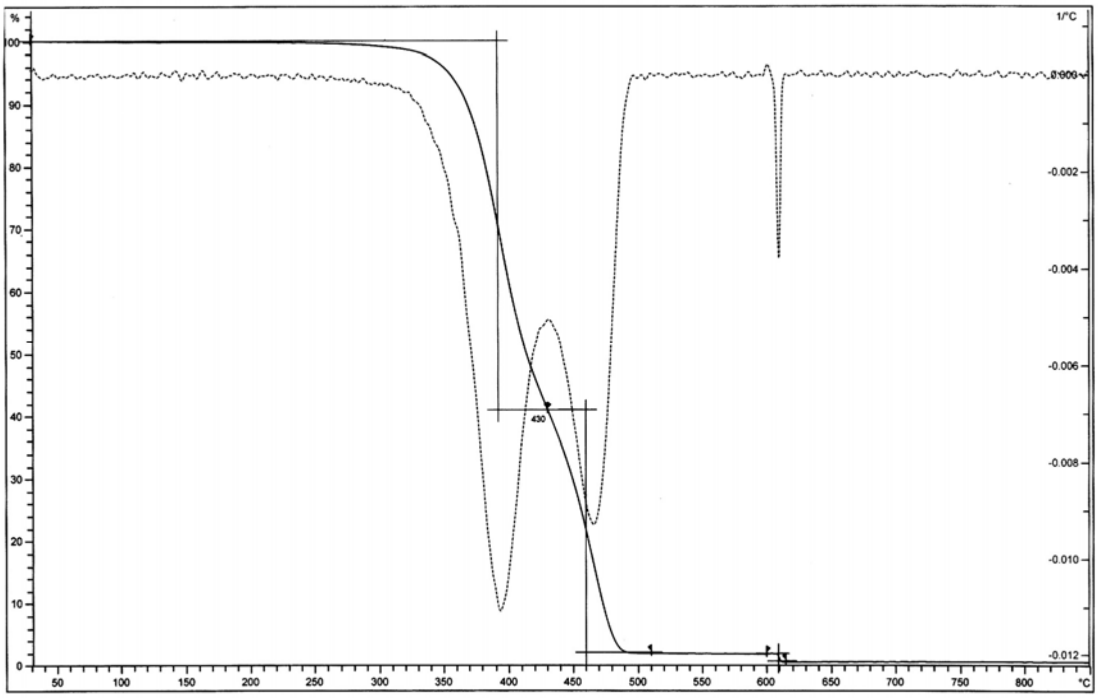


Figure D-18 TGA thermogram of HDPNR XVII

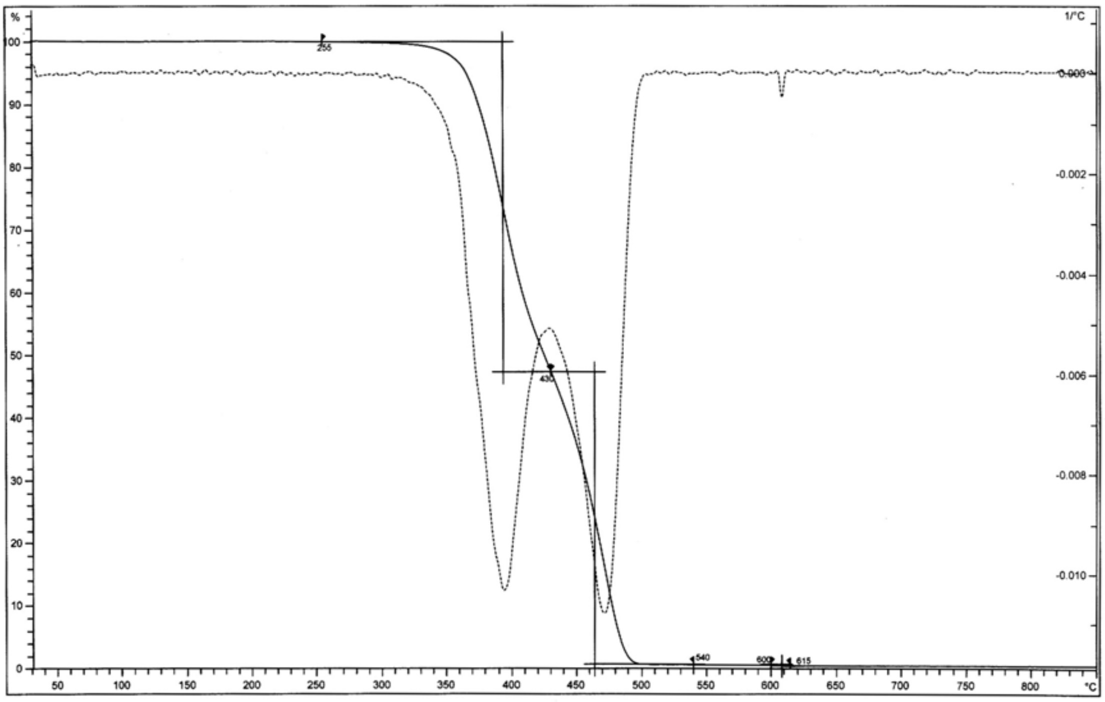


Figure D-19 TGA thermogram of HDPNR XVIII

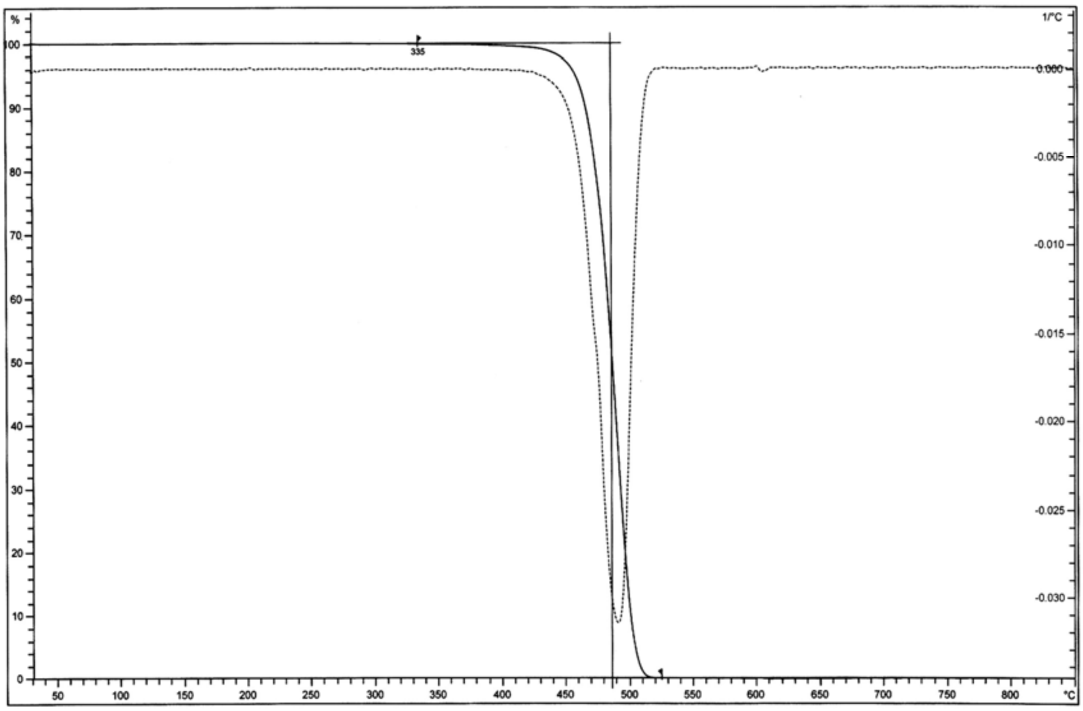


Figure D-20 TGA thermogram of EPDM I

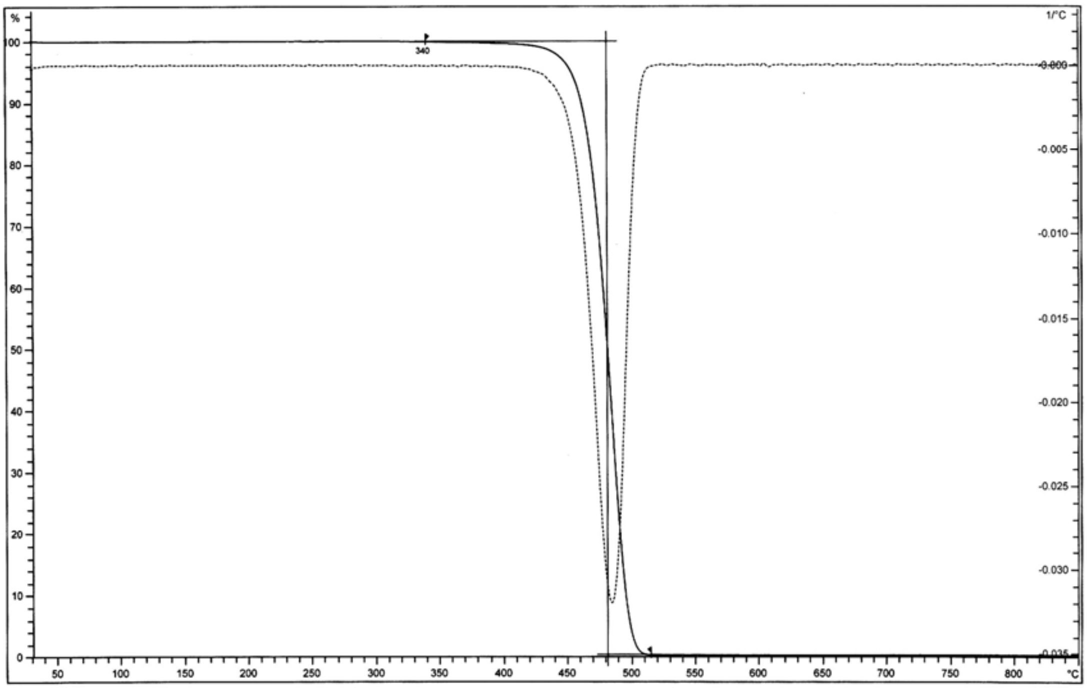


Figure D-21 TGA thermogram of EPDM II

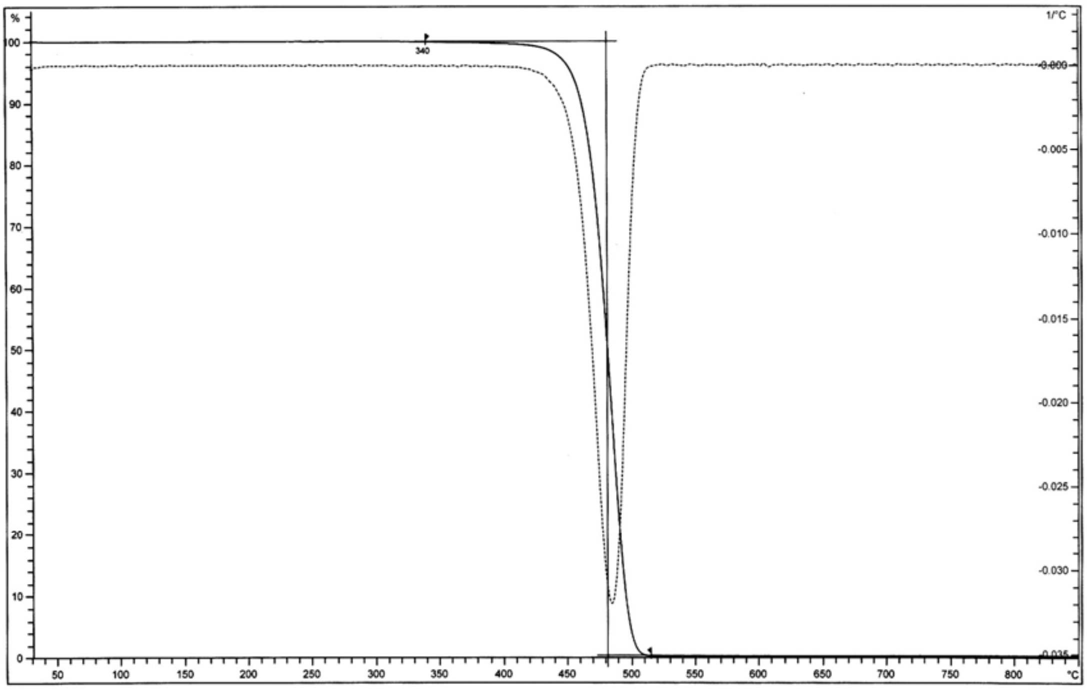


Figure D-22 TGA thermogram of EPDM III

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