พอลิเมอไรเซชันของ 1,3-บิวทาไดอีนโดยใช้ตัวเร่งปฏิกิริยาโคบอลต์/นีโอดีเมียมและนิกเกิล/นีโอดีเมียม

นางจันทร์สุรีย์ ชาติอาษา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาปิโตรเคมี
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ปีการศึกษา 2557

POLYMERIZATION OF 1,3-BUTADIENE USING
Co/Nd AND Ni/Nd CATALYSTS

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Petrochemistry
Faculty of Science
Chulalongkorn University
Academic Year 2014

Thesis Title	POLYMERIZATION OF 1,3-BUTADIENE USING Co/Nd AND Ni/Nd CATALYSTS
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จันทร์สุรีย์ ชาติอาษา : พอลิเมอไรเซชันของ 1,3-บิวทาไดอีนโดยใช้ตัวเร่งปฏิกิริยาโคบอลต์/นีโอดีเมียมและนิกเกิล/นีโอดีเมียม (POLYMERIZATION OF 1,3-BUTADIENE USING Co/Nd AND Ni/Nd CATALYSTS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. นพิดา หิญชีระนันทน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ศ. ดร. ภัทรพรรณ ประศาสน์สารกิจ, Prof. Dr. Garry L. Rempel, 88 หน้า.

ยางบิวทาไดอีนเกรดการค้าซึ่งสังเคราะห์ได้จากการทำปฏิกิริยาพอลิเมอไรเซชันของ 1,3 บิวทาไดอีน ด้วยตัวเร่งปฏิกิริยานีโอดีเมียมซีเกลอร์-แนตตา ((Nd)-based Ziegler-Natta catalyst) กับสารประกอบแอลคิลอลูมิเนียมเฮไลด์ (alkylaluminium halides) ทำหน้าที่เป็นตัวเร่งปฏิกิริยาร่วม ให้โครงสร้างแบบซิส-1,4 ปริมาณ 97-99% ที่สูงกว่ายางบิวทาไดอีนที่ผลิตจากระบบตัวเร่งปฏิกิริยานิกเกิล (Ni) หรือโคบอลต์ (Co) นอกจากนี้ระบบตัวเร่งปฏิกิริยานีโอดีเมียม ให้ร้อยละการเปลี่ยนแปลงมอนอเมอร์สูงถึง 100% โดยไม่มีเจลเกิดขึ้นในผลิตภัณฑ์และให้ไวนิลไซโคลเฮกซีน (cyclohexene) น้อยมาก อย่างไรก็ตามยางบิวทาไดอีนที่ได้จากตัวเร่งปฏิกิริยานีโอดีเมียม มีความหนืดสูงไม่เหมาะในการผลิตพอลิอะคริโลไนไทรล์บิวทาไดอีนสไตรีน (polyacrylonitrile-butadiene-styrene, ABS) ยางบิวทาไดอีนที่สังเคราะห์จากตัวเร่งปฏิกิริยานีโอดีเมียมมีการไหลย้อยสูงทำให้ยากต่อการอัดรีด (poor extrudability) เนื่องจากยางบิวทาไดอีนที่ผลิตจากตัวเร่งปฏิกิริยานิกเกิล (Ni-BR) และ โคบอลต์ (Co-BR) มีโครงสร้างแบบกิ่ง (branching) มากกว่าทำให้ง่ายต่อการอัดรีด อย่างไรก็ตามระบบตัวเร่งปฏิกิริยานิกเกิลและโคบอลต์จำเป็นต้องใช้ ไตรเอทิลอลูมินัม (triethylaluminum, TEAL) และไดเอทิลอลูมินัม (diethylaluminum, DEAC) เป็นตัวเร่งปฏิกิริยาร่วม ดังนั้นวัตถุประสงค์ของงานวิจัยนี้คือการรวมข้อดีของระบบตัวเร่งปฏิกิริยาเหล่านี้มาผลิตยางบิวทาไดอีนที่มีโครงสร้างแบบซิส-1,4 สูง มีสมบัติเชิงกลที่ดีและง่ายต่อการขึ้นรูป ผลการศึกษาแสดงให้เห็นว่าการใช้ตัวเร่งปฏิกิริยานีโอดีเมียมผสมกับโคบอลต์ (Co/Nd) และนีโอดีเมียมผสมกับนิกเกิล (Ni/Nd) โดยใช้ไตรเอทิลอะลูมินัมและไดเอทิลอะลูมินัม ในไซโคลเฮกเซน ให้ร้อยละการแปลงมอนอเมอร์ 90% และ 100% ตามลำดับ ยางบิวทาไดอีนที่ได้มีโครงสร้างแบบซิส-1,4 สูงในปริมาณมากกว่า 97% และมีโครงสร้างไวนิล-1,2 ที่ต่ำ (0.14-0.40%) มีคุณสมบัติเชิงกลที่ดีและการทนทานต่อการสึกหรอดีกว่ายางบิวทาไดอีนเกรดการค้าจากระบบตัวเร่งปฏิกิริยาโคบอลต์หรือนิกเกิล

สาขาวิชา ปิโตรเคมี
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ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
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5273910723 : MAJOR PETROCHEMISTRY

KEYWORDS: BUTADIENE / NEODYMIUM / COBALT / NICKEL / POLYMERIZATION / MICROSTRUCTURE

CHANSUREE CHATARSA: POLYMERIZATION OF 1,3-BUTADIENE USING Co/Nd AND Ni/Nd CATALYSTS. ADVISOR: ASST. PROF. NAPIDA HINCHIRANAN, Ph.D., CO-ADVISOR: PROF. PATTARAPAN PRASASSARAKICH, Ph.D., PROF. GARRY L. REMPEL, Ph.D., 88 pp.

Commercial butadiene rubber (BR) synthesized from 1,3-butadiene (BD) polymerization using neodymium (Nd)-based Ziegler-Natta catalyst coordinated with alkylaluminium halides as co-catalysts contains 97-99 % *cis*-1,4 configuration, which is higher than BR produced from Ni- or Co- based catalyst system: Moreover, the Nd-based catalyst provides 100% BD conversion without gel formation in the obtained BR product and this system ฟสหน produces less vinyl-cyclohexene content. However, the BR obtained from Nd-based catalyst (Nd-BR) has high viscosity, which is inappropriate for the production of poly(acrylonitrile-butadiene-styrene) (ABS). The Nd-BR also has high cold flow properties inducing poor extrudibility. Since BR produced from Ni- (Ni-BR) and Co-based catalyst (Co-BR) has higher degree of branching, it results in better processability. However, Ni- and Co-based catalysts require triethylaluminum (TEAL) and diethylaluminum chloride (DEAC) as co-catalysts. Therefore, the objective of this research is to combine the advantage of these catalysts to produce BR with high content of *cis*-1,4 structure, good mechanical properties and easy processing. The results showed that the use of Nd mixed with Co (Co/Nd) and Nd mixed with Ni (Ni/Nd)- based catalyst systems coordinated with TEAL and DEAC in the presence of cyclohexane provided 90% and 100% BD conversion, respectively. The obtained BR had content of *cis*-1,4 configuration higher than 97% and low amount of *vinyl*-1,2 unit (0.14-0.40%) with the greater mechanical properties and abrasion resistance than the commercial BR produced by using Co- or Ni- based catalyst.

Field of Study: Petrochemistry
Academic Year: 2014

Student's Signature ....
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ACKNOWLEDGEMENTS

The author would like to express sincere appreciation and deep thankfulness to her advisor, Asst. Prof. Dr. Napida Hinchiranan, and co-advisors, Prof. Dr. Garry L. Rempel and Prof. Dr. Pattarapan Prasassarakich, for their helpful discussion, encouraging guidance, supervision and support throughout her research. The author would like to acknowledge Assoc. Prof. Dr. Supawan Tantayanon, Assoc. Prof. Dr. Wimonrat Trakarnpruk, Assoc. Prof. Dr. Nuanphun Chantarasiri and Assoc. Prof. Dr. Kitikorn Charmondusit for their contribution as the dissertation chairman and members of thesis committee, who have rendered worthy comments and suggestions.

The author also acknowledges to Bangkok Synthetic and BST Elastomer Co., Ltd (Thailand) for financial support and all kinds of equipment.

Many thanks also go to the Program of Petrochemistry and Polymer Science and the Department of Chemical Technology, Faculty of Science, Chulalongkorn University, and the Department of Chemical Engineering, University of Waterloo, Canada, for providing research facilities throughout this research work.

Finally, the author would like to express her deep sense of gratitude to her family, for their love, support and encouragement throughout this graduate study. Also, special thanks are extended to her boss for friendship, support and encouragement.

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LIST OF ABBREVIATIONS

ABS : Acrylonitrile butadiene styrene rubber
BD : 1,3-Butadiene
BF_3 : Boron trifluoride
BMP : 2,6-di-tert-butyl-4-methyphenol
BR : Butadiene rubber
Br : Bromide
Cl : Chloride
Co : Cobalt
Co-BR : Butadiene rubber obtained by cobalt catalysis
Co/Nd-BR : Butadiene rubber obtained by cobalt and neodymium catalysis
DEAC : Diethylaluminum Chloride
DIBAH : Di-isobutylaluminum Hydride
DMA : Dynamic Mechanical Analysis
DSC : Differencial Scanning Calorimetry
Ea : Activation Energy
EASC : Ethylaluminum Sesquichloride
F : Fluoride
FTIR : Fourier Transform Infrared Spectroscopy
GPC : Gel Permeation Chromatography
HF : Hydrogen Fluoride
HIPS : High Impact Polystyrene
IRB : Industry Reference Black
M_H : Maximum Torque
M_L : Minimum Torque
Mw : Molecular Weight
MWD : Molecular Weight Distribution
Nd : Neodymium
Nd-BR : Butadiene rubber obtained by neodymium catalysis

LIST OF ABBREVIATIONS (continued)

NdA	:	Neodymium Neopentanoate
NdP	:	Neodymium bis(2-ethylhexyl) phosphate
NdV_3	:	Neodymium Versatate
Ni	:	Nickel
Ni-BR	:	Butadiene rubber obtained by nickel catalysis
Ni/Nd-BR	:	Butadiene rubber obtained by nickel and neodymium catalysis
NMR	:	Nuclear Magnetic Resonance Spectroscopy
NR	:	Natural Rubber
phr	:	Part Per Hundred of Rubber
PPA	:	Polyoxyethylene Alkyl Phenyl Ether
ppm	:	Part Per Million
rpm	:	Revolution Per Minute
TBBS	:	n-Tert-Butyl-Benzothiazone Sulfonamide
tc90	:	Optimum Cure Time
ts_1	:	Scorch Time
TEAL	:	Triethylaluminum
THF	:	Tetrahydrofuran
Tg	:	Glass Transition Temperature
Ti	:	Titanium
TIBA	:	Triisobutylaluminum
$TiCl_4$	:	Titanium Tetrachloride
Tm	:	Melting Temperature
TSC	:	Total Solid Content
ZnO	:	Zinc Oxide
4-VCH	:	4-Vinyl Cyclohexene

CHAPTER I

INTRODUCTION

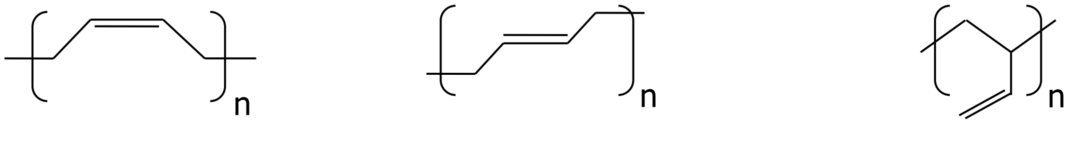
1.1 Motivation

Due to the current energy crisis, tire manufactures have to develop new tires with high performance by reducing energy dissipation or rolling resistance [1]. Moreover, such tires need to have high traction during braking and high abrasion resistance [1]. Polybutadiene rubber (BR) is mostly used in the tire industry [2]. Commercial BR with high *cis*-1,4 configuration is important since this structure is similar to that of natural rubber (NR) and provides excellent dynamic properties and good resistance for abrasion and low temperature environments. These properties are related to the development of tires with high energy saving performance to reduce fuel consumption. In industrial production of BR, the use of Ziegler/Natta catalysts based on nickel (Ni), cobalt (Co) and titanium (Ti) coordinating with organoaluminum compounds produces BR with 93-97% *cis*-1,4-configuration [3]. Recently, BR containing 99% *cis*-1,4 microstructure has been produced by using lanthanide catalysts based on neodymium (Nd) coordinating with aluminum halides acting as co-catalysts [3, 4], The lanthanide catalysts also have high solubility in saturated hydrocarbon solvents, which are safer and more environmental friendly than aromatic solvents such as benzene and toluene used in 1,3-butadiene (BD) polymerization [4]. Moreover, the lanthanide catalysts promote high monomer conversion (ca. 100%) without any gel formation and also give less production of vinyl cyclohexane, which is a dimer of butadiene [5]. However, the lower activity of Nd than that of Ni- or Co-based Ziegler/Natta catalyst systems for BD polymerization is a disadvantage. Nd is also more expensive than the traditional Ziegler-Natta catalysts and its price is also dependent on China, which is the largest Nd producer [4, 5]. The conventional BR process generally uses Co- or Ni-based Ziegler-Natta catalysts coordinating with diethyl aluminum chloride (DEAC) and triethyl aluminum (TEAL), respectively. However, the price of alkyl-aluminum compounds is the major cost of these Ziegler/Natta catalysts and they also require special techniques to be handled for safely [6, 7]. In addition, the BR obtained from Co and Ni-based catalysts has a higher polydispersity and branching content than that from the Nd-based catalyst. A BR with high level of polydispersity and chain branching is easier for processing than that of highly linear BR obtained from the Nd-based catalyst [8]. With respect to economic aspects, safety concerns and processability, BD polymerization catalyzed by mixed catalysts: transition metal and lanthanide coordinating with commercial co-catalysts have been attractive.

1.2 History and Technology of Butadiene Rubber

In 1910, BD polymerization was discovered by the Russian chemist “Sergei Vasilyevich Lebedev” [9]. The production of BR using sodium as a catalyst was also developed in 1928 [9]. In 1930, BR was used as an alternative rubber to replace natural rubber (NR) in the Soviet Union and it was manufactured in the first pilot plant. In the mid-1950s, a large scale commercial BR production resulted after the discovery of the Ziegler-Natta catalyst. For tire manufacture, this catalyst system was much better than the old sodium catalyst [9].

The worldwide consumption of BR was about 2.8 metric tons in 2010. It has been forecast to increase to 4.0% from 2010-2015 [10]. BR is mostly synthesized via solution polymerization. BD gas is dissolved in hydrocarbon solvents and is catalytically polymerized using anionic or Ziegler-Natta catalysts. BR is mainly classified based on its microstructure as 3 types: *cis*-1,4, *trans*-1,4 and *vinyl*-1,2 configurations as demonstrated in Figure 1.1 [5]. Each microstructure results in a BR with different properties. For example, BR with a high content of *cis*-1,4 structure has high elasticity, whereas BR with a high amount of *trans*-1,4 configuration exhibits a plastic crystal property, which is used in a few applications. For the *vinyl*-1,2 structure, its content in BR is typically less than a few percent [9]. In addition, the different microstructure of BR induces the different levels of branching, molecular weights and glass transition temperature (T_g) as shown in Table 1.1.



cis-1,4-Poly(butadiene) *trans*-1,4-Poly(butadiene) *vinyl*-1,2-poly(butadiene)

Figure 1.1 Microstructures of BR.

Table 1.1 Glass transition and melting temperature of BR with different Microstructures [11].

BR	T_g,°C	T_m,°C
1,4-*cis*-	- 106	2
1,4-trans-	- 107	-
1,2-syndiotactic	- 28	156
1,2-isotactic	-	126
1,2-atactic	- 4	-

BR containing a high content of *cis*-1,4 configuration has the lowest T_g, which enables it to be handled in a very low temperature environment. Thus, it is more favorable to be applied in various industries. Moreover, it has a strain-induced crystallization property to promote better green strength with a highly effective tackiness compared to other rubbers. This structure also provides other excellent properties such as low heat built-up and high resilience including high abrasion resistance [5, 9], which is required for the green tire industry since it can decrease fuel consumption. Commercial BR can be classified into 5 types according to its microstructure as shown in Table 1.2

Table 1.2 Typical microstructures of BR [12].

	Structure (%)		
Name	*Cis*-1,4-	*Trans*-1,4-	*Vinyl*-1,2-
High-*cis*	93-98	1-3	1-4
Medium-*cis*	42	48	10
Medium-*vinyl*	27	31	42
High-*vinyl*	15-18	10-12	70-75
Very high-*vinyl*	1	1	98

However, the well-known BRs in the market place have low *cis*-1,4 content (40%) and high *cis*-1,4 content (> 93%) [12]. It has been believed that BR with a higher amount of *cis*-1,4 structure provides a greater improvement in elastic properties [13]. The microstructure of BR is dependent on the applied catalyst system [14]. Details for each type of BR are reported as follows: High *cis*-1,4 BR [8, 14]. This BR type has a high proportion of *cis*-1,4 units (typically > 92%) with a small amount of *vinyl*-1,2 structure (< 4%) [8, 14]. It is normally manufactured using Ziegler-Natta catalysts based on transition metals. When Co is used as the catalyst for BD polymerization, the obtained BR has a high degree of branching resulting in a low viscosity and is of low mechanical strength. For the Ni-based catalyst, the BR obtained has an intermediate level of branching. The use of Nd as the BD polymerization catalyst gives BR having a high linear structure with a high percentage of 98% *cis*-1,4 units providing superior mechanical strength.

Medium *cis-1,4* BR [12-14]: This BR usually contains 36% *cis*-1,4, 54% *trans*-1,4 and 10% *vinyl*-1,2 configurations. It is produced by BD polymerization using an alkyl lithium (e.g. butyllithium) catalyst. Because of its high liquid-glass transition, the BR containing a low content of *cis*-1,4 structure is not used in tire manufacturing. However, it can be advantageously applied as an additive in plastics due to its low gel content.

Medium and high *vinyl*-1,2 BR [9]: This BR contains a high amount of *vinyl*-1,2 configuration (> 70%) with a high glass transition temperature. It has been produced by using an alkyllithium catalyst, which was discovered in 1980 by researchers from Zeon Company, Japan. Moreover, Firestone, an American company, as well as Japan Synthetic Rubber (JSR), have produced high *vinyl*-1,2 BR containing 90% *vinyl*-1,2 content. The obtained BR has elastic properties at room temperature and it can transform as a liquid at high temperatures providing an advantage in injection molding.

In addition, BR can also be classified according to the polymerization technology and initiator/catalyst as 6 types [5]: (1) emulsion-BR (radical polymerization in aqueous emulsion, E-BR), (2) lithium-BR (anionic polymerization in solution, Li-BR), (3) cobalt-BR (coordinative polymerization in solution, Co-BR),

(4) titanium-BR (coordinative polymerization in solution, Ti-BR), (5) nickel-BR (coordinative polymerization in solution, Ni-BR) and (6) neodymium-BR (coordinative polymerization in solution, Nd-BR). The solution process consisting of solvent, catalyst and monomer is the most favorable for production of BR. It has been developed for manufacturing high *cis*-BR (> 90%) during the last half of the 1950s paralleled with the production of styrene-butadiene rubber (SBR) and *cis*-1,4 polyisoprene processes [12]. High *cis*-1,4 BR production, using initiator systems, requires careful handling since the initiators are very sensitive to various impurities such as water, oxygen, sulfur, and/or acetylenic compounds. An appropriate hydrocarbon solvent is also required [12].

1.3 Properties and Application of High Cis-1,4 Butadiene Rubber

High *cis*-1,4 BR has outstanding properties, for use in many applications, such as high abrasion resistance (good tread wear), low rolling resistance (less fuel consumption), low heat generation (low heat build-up),and a low T_g value. It is also superior to many polymers in resisting cut growth and flex cracking [15]. The major applications of BR are divided into 4 categories: tires, thermoplastics, technical rubber goods and golf ball. Figure 1.2 shows that the manufacturing of tires accounts for the major segment in consuming BR (ca. 70%) of the polymeric constituents for producing treads, retread rubber, tire carcasses, and tire side walls for trucks and automobiles [15, 16]. Moreover, BR is also used as an impact modifier for polystyrene -acrylonitrile-butadiene–styrene resin (ABS)(ca. 17%) of the total BR consumption. However, *cis*-1,4 BRs has poor properties for wet traction. Most BRs are blended with other rubbers to enhance processability.

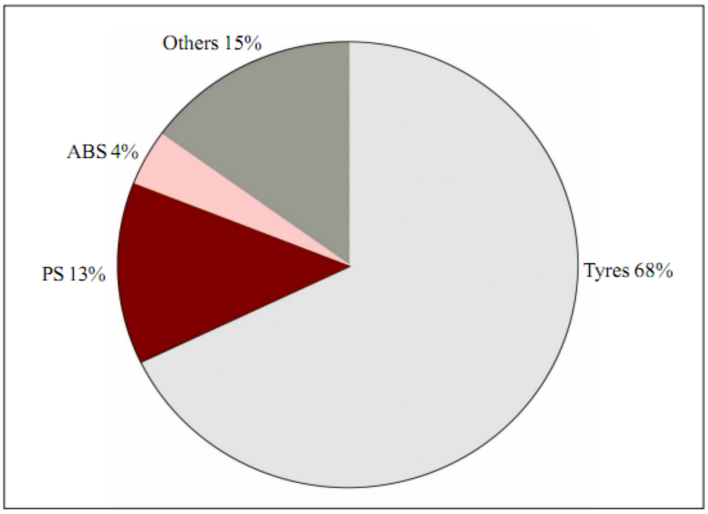


Figure 1.2 Global BR applications [17].

In recent years, as a counter measure for global warming and environmental protection, the awareness of the resource and energy conservation has increased. In the automobile industry, various measures related to energy conservation are being attempted. Since automobile components; especially, tires account for 2/3 of rubber parts [3]. BR is used in various parts of tires as shown in Figure 1.3 [17]. Thus, the rubber industries have tried to develop catalysts and also use safer and more environmentaly friendly solvents to produce very high *cis*-1,4 BR for the production of high performance tires which provide fuel savings, low energy dissipation or low rolling resistance, high traction during braking and high wear resistance (low weight loss during abrasion) [18]. Figure 1.4 illustrates the history of the most important trends in the study and development of BR for tire applications [19]. It shows that BR with a high *cis*-14 configuration provides improved tire performances providing 30%, 28% and 21% better rolling resistance, skid resistance and abrasion resistance as well as heat build-up, respectively.

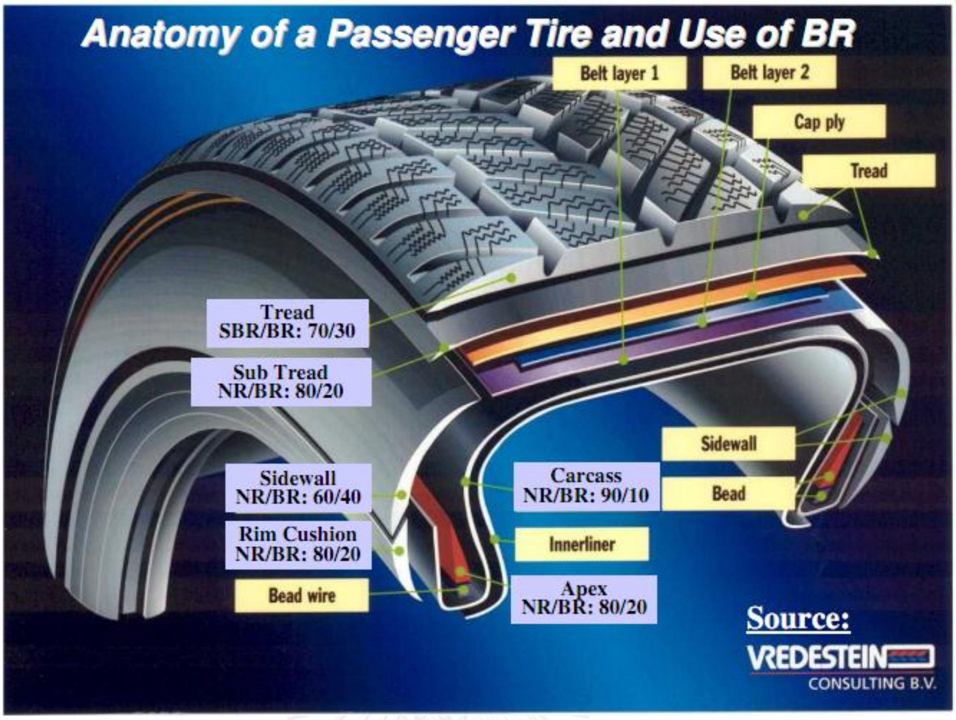


Figure 1.3 Application of BR for tire production [17].

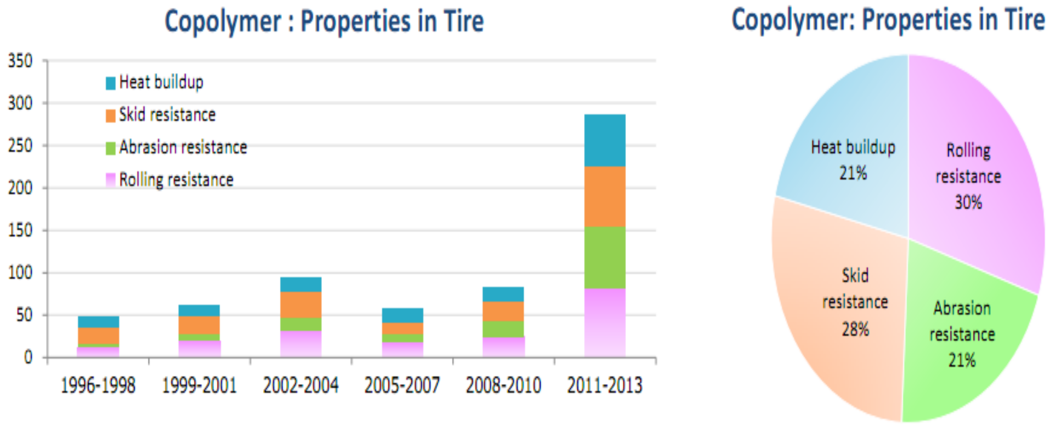


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Figure 1.4 BR properties for tire [19].

1.4 Ziegler-Natta Type Catalysts for High *Cis-1,4* Butadiene Rubber Production

Ziegler-Natta catalysts are composed of a combination of alkyl aluminum or aluminum hydride and transition metal compounds [20]. They have been developed to produce high *cis-1,4* BR since the mid-1950s [9, 13]. This catalyst type exhibits a high degree of chemoselectivity and stereoselectivity [21]. Furthermore, it provides a BR with better performance than a BR produced by using the sodium catalyst. The first company producing high *cis*-1,4 BR using a Ziegler-Natta catalyst was Goodyear tire and B.F. Goodrich [9]. Currently, there are at least four different types of Ziegler-Natta catalysts used for BR production on the industrial scale [11]. There are based on titanium (Ti), cobalt (Co), nickel (Ni) and the rare earth metal neodymium (Nd) [8]. These catalysts produce BR with different microstructures providing a difference in its molecular weight (MW), molecular weight distribution (MWD) and degree of chain branching [11]. The microstructure in BR obtained from each catalyst system is considered for various applications [14]. Commercially applied Ziegler/Natta–catalysts for BR production are presented in Table 1.3. The detail of each system is stated below:

Titanium catalysts: Phillips Petroleum was the first company using a heterogeneous titanium catalyst system to produce *cis*-1,4 BR in the 1950s. This system produces BR with low branching content and narrow MWD leading to good tensile properties and fatigue resistance. However, its processibility is poor. The catalyst system consisting of a titanium halide precursor and an aluminum alkyl as a co-catalyst produces BR with > 90% of c*is-1,4* content. Although the catalytic activity is sensitive to the Al/Ti ratio, the overall *cis-1,4* content in BR is only slightly affected. The microstructure of the obtained BR especially *cis*-1,4 configuration is very sensitive to the type of halogen employed in the polymerization. Table 1.4 shows that the *cis*-1,4 content significantly decreases as iodide is replaced with more electronegative halides [3, 11]. The effect of halideon microstructure in BR appears for all of the *cis*-specific transition metal catalysts except Nd. Commercially, the triisobutylaluminum (TIBA)/iodine (I_2)/titanium tetrachloride ($TiCl_4$) system has been used to produce *cis*-1,4 BR with optimized conversion and MW. The synthesis of high *cis*-1,4 BR was first commercially produced in Europe and USA.

Table 1.3 Commercial Ziegler/Natta-catalysts in BR production [5].

Catalyst system (molar composition)	Conc. of metal M (mg/L)	BR Yield/ Kg(BR). g-1(M)	*cis*-1,4 %	*trans1,4* %	*vinyl*-1,2 %	MWD	T_g (^oC)
$TiCl_4/I_2/\ Al^iBu_3$ (1/1.5/8)	50	4-10	93	3	4	medium	-103
$Co(OCOR)_2/\ H_2O/\ AlEt_2Cl$ (1/10/200)	1-2	40-160	96	2	2	medium	-106
$Ni(OCOR)_2/\ BF_3\text{-}OEt_2/\ AlEt_3$ (1/7.5/8)	5	30-90	97	2	1	broad	-107
$Nd(OCOR)_3/\ Et_3AlCl_3/\ Al^iBu_2H$ (1/1/8)	10	7-15	98	1	1	very broad	-109

Table 1.4 Effect of metal halides and transition metals on cis-1,4 content (%) in BR.

Transition Metal	I	Br	Cl	F
Titanium	93	87	75	35
Cobalt	50	91	98	93
Nickel	10	80	85	98
Neodymium	97	97	96	96

Cobalt catalysts: The cobalt (Co) catalyst first used to produce high *cis*-1,4 BR was revealed by B.F. Goodrich. The BR obtained has a high degree of branching and good processibility with low mechanical strength [9]. In earlier research work, Co species in of the form of $CoCl_2$ was used as the catalyst precursor coordinated with trialkyl aluminum species; however it did not provide a good active catalyst [11]. In the Co catalyst system, an alkyl aluminum halide acts as the co-catalyst to generate an active catalyst. This catalytic activity is related to the Lewis acidity of the co-catalyst [22]. For example, the use of aluminum ethyl sesquichloride [$Al_2(C_2H_5)_3Cl_3$] provided a highly active catalyst. However, it was found that the increase in the strength of the Lewis acid induced gel formation during the process [9]. A balance of activity and gel content has been achieved through the use of water as a third catalyst component. It is found that the degree of branching, reflecting the solution viscosity at equal molecular weight, decreased with increasing water content. Figure 1.5 shows a mechanism for the Co-based catalyst to synthesize BR proposed by Ledwith and Sherrington in 1973 [22]. Moreover, a typical *cis*-1,4 content is in the range from 95 to 98%. The catalyst activity and MW of the obtained BR are also dependent on the solvent used for polymerization. Benzene is the most suitable solvent for BD polymerization using this Co-based catalyst. However, mixtures of aromatic and aliphatic solvents for large scale BR production have been favored in order to reduce the amount of benzene emissions. A variety of Co compounds such as $CoCl_2$, $Co(acac)_2$ and cobalt carboxylate etc. has been used as catalyst precursors. However, only soluble compounds such as cobalt octoate or cobalt naphthenate have been commercially applied.

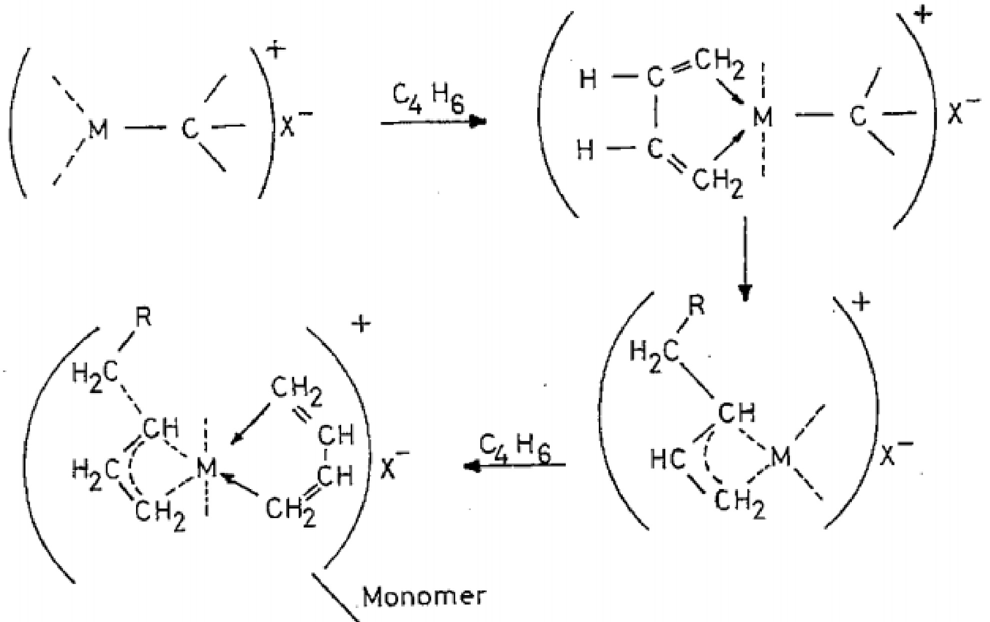


Figure 1.5 Cobalt based catalyst mechanism proposed by Ledwith and Sherrington [22].

Nowadays, BR produced using a Co-based catalyst system consisting of cobalt (II) octanoate, diethyl aluminum chloride (DEAC) and water used as an activator have been commercialized [23, 24]. The obtained BR (Co-BR) with a high level of branching and low solution viscosity is appropriate for the production of acrylonitrile-butadiene-styrene (ABS) and high impact polystyrene (HIPS) [2, 5, 8]. Moreover, the high content of branching can decrease the cold flow effect of uncured BR to provide ase of preparation in rubber compounding and making rubber solutions [2, 5]. However, the drawback of Co-BR is crosslinking resulting in gel formation, which greatly affects the process behavior and surface appearance of the extruded products [23]. It also has a long optimum cure time (t_{90}) and low tackiness [2]. Moreover, the low solubility of applied water as the activator for Co/DEAC in solution polymerization induces instability of the process [23].

Nickel Catalysts: In 1963, Bridgestone Tire reported that the BD polymerization could not be achieved when nickel (Ni) was applied in metallic state. When nickel was supported by silica-alumina or diatomaceous earth or mixed with halogenated materials such as boron trifluoride or titanium tetrachloride, *cis*-1,4 BR was formed. Finally, it was found that *cis*-1,4 polybutadiene can be obtained from a system of nickel in the metallic state combined with acid content or a system containing an organic chloride of nickel or an organometallic compound including reduction and acid content [25]. This catalyst provided a BR with high cis-1,4 configuration (97-98%). In the same year, JSR used the highly active catalyst system $(Ni(OOC_8H_{15})_2/BF_3.O(C_2H_5)_2/Al(C_2H_5)_3$ to produce BD [25]. Then, it was commercialized by Bridgestone Tire & JSR in 1964 [2]. It is believed that the control point of stereoregurality of BD is due to elemental Ni. Throckmorton et al. [26] studied the HF-Nickel-R_3Al catalyst system to produce high *cis*-1,4 BR and it was found that HF was the only hydrogen halide to promote Ni to produce the desired stereoregular BR. This indicated that fluorine played a very important role, perhaps affecting the entry of the monomer or catalyst sites on the Ni or both [26]. Figure 1.6 shows the proposed reaction mechanism for this catalyst system [26]. The Ni-BR typically contains less branching than the commercial Co-BR, but both Ni-BR and Co-BR have an equal high *cis*-1,4 content (ca. 98%). The obtained BR also shows a large molecular weight distribution of 4-5 indicating good processibility with less bagging on a mill [11, 26]. The commercial process utilizes a soluble nickel (II) carboxylate, aluminum trialkyl, and a halogen source. The microstructure of BR obtained from this process is dependent on the choice of halogen. From Table 1.4, the use of nickel-iodide yields mostly *trans*-1,4 BR while Br, Cl, and F all favor *cis* polymerization [11, 12]. The catalyst activity of the Ni-based catalyst system is similar that of Co in terms of reaction rate and molecular weight of BR. However, the Co catalyst promotes chain transfer to readily compete with propagation resulting in a broad molecular weight distribution. Moreover, studies with nickel octanoate have shown that the microstructure is a function of molecular weight. As molecular weight increases the *cis* content increases at the expense of both the *trans* and *vinyl content*; the amount of trans is always about twice the amount of vinyl. The Ni catalyst generally used in industrial scale BD production is nickel naphthenate in conjunction with boron fluoride etherate and trialkylalumimium [27]. However, this process generates vinyl cyclohexene, which is harmful to the environment [4]. In addition, the use of boron trifluoride in the Ni-based catalyst system produces strong acid when it comes in contact with water, leading to equipment corrosion and gel-formation in the BR product [28]. Due to the high gel content of Ni-BR, its application is limited to the production of high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene resins (ABS) [5]. Thus, BR with a high degree of branching produced from the Ni-based catalyst has better processability with lower tensile strength and fatigue resistance [14].

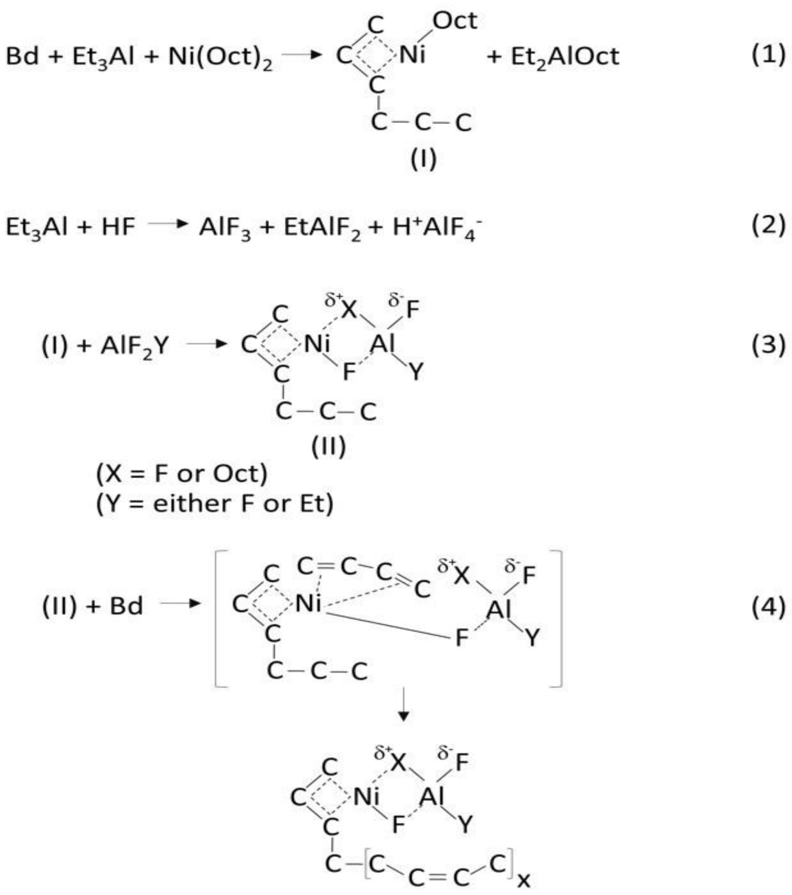


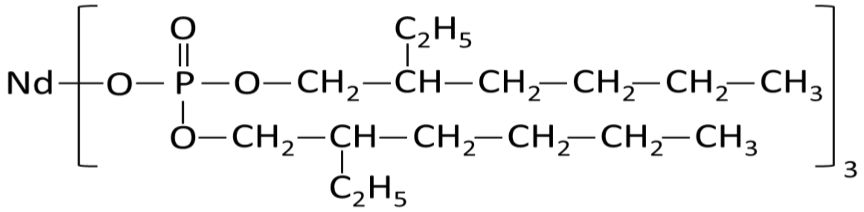
Figure 1.6 Proposed reaction mechanism of Ni based catalyst [26].

Neodymium Catalyst: BR containing 99% *cis*-1,4 microstructure can be produced by using a lanthanide catalyst based on neodymium (Nd) coordinating with aluminum halides acting as co-catalysts [5]. Nd complexes have been found to be more favorable than other lanthanides for application as a catalyst for polymerization due to its higher activity using a reasonably priced precursor. It also gives less dimer formation during polymerization than the conventional system in the following order: Nd < Ni < Ti [5]. The Nd catalysts also have high solubility in saturated alkanes, which are safer and more environmental friendly than benzene and toluene which are generally used as solvents for BD polymerization. Moreover, the Nd catalysts promote high monomer conversion (ca. 100%) without gel formation in the resulting BR product. In addition, the catalyst residue in the final polymer product does not affect the BR after thermal aging. As mentioned above, many researchers have attempted to increase the level of *cis*- 1,4 configuration in BR by focusing on the Nd catalyst and co-catalyst concentrations, ageing condition and solvent type used in the polymerization. Moreover, the performance of high *cis*-1,4 polybutadiene has been investigated. These have been reported in selected previous literature and patents as described below:

Effect of Nd complexes and co-catalyst

Friebe et al. [29] compared the reactivity of catalysts such as neodymium versatate (NdV_3), neodymium neopentanolate (NdA) and neodymium bis (2-ethylhexyl) phosphate (NdP) (Figure 1.7) in Ziegler-Natta catalyst systems for BD polymerization. Di-isobutylaluminum hydride (DIBAH) and ethyaluminum sesquichloride (EASC) were used as the co-catalyst and a chlorinating agent, respectively. It was reported that the reactivity of NdV_3/DIBAH/EASC system at a nCl/nNd molar ratio of 2 and the nDIBAH/$nNdV_3$ molar ratio of 30. The NdP gave the highest reactivity at nDIBAH/nNdP of 5, whereas, NdA had the lowest reactivity. For all catalysts, the amount of *cis*-1,4 microstructure in the BR obtained decreased except for nDIBAH/nNd. The highest *cis*-1,4 content (ca. 97.6%) was achieved when NdP was used at a nDIBAH/nNdP molar ratio of 5 and nCl/nNdP molar ratio of 2.

NdV_3 NdA



NdP

Figure 1.7 Structures of NdV_3, NdA and NdP.

Oehme et al. [30] studied the homopolymerization and copolymerization of BD catalyzed by Nd coordinating with diethylaluminum chloride, triethylaluminum in the presence of hexane. It was found that the increase in the mole ratio of diethyl chloride yielded a maximum conversion of 95%. The *cis* -1,4-configuration content in BR also increased from 86 to 94 % by reducing the triethylaluminum/neodymium octoate molar ratio.

Rocha et al. [31] reported that the content of *cis*-1,4 microstructure decreased from 98 to 95% by increasing the Al/Nd molar ratio. The activity of catalyst was related to the length of the alkyl group in the aluminum compounds and the reactivity increased in following order: tri(n-octyl)aluminum > tri(n-hexyl)aluminum > tri(i-butyl)aluminum > di(i-butyl)aluminum hydride.

Ferreira et al. [32] studied the effect of the Cl/Nd molar ratio on BD polymerization. The chloride sources in this study were *t*-butyl chloride (*t*-BuCl), ethylaluminum sesquichloride (EASC) and diethylaluminum chloride (DEAC). The results showed that DEAC exhibited higher activity than EASC and *t*-BuCl. However, *t*-BuCl gave BR with a high molecular weight and *cis*-1,4-microstructure.

Effect of catalyst aging

Coutinho et al. [33] studied the effect of Nd catalyst aging on the catalyst activity, monomer conversion, microstructure and molecular weight of the BR obtained. It was found that the catalyst activity decreased with increasing ageing temperature due to the thermal degradation of thecatalyst. However, the ageing time did not affect the stereo-selectivity of the active sites of the catalyst. The *cis*-1,4 content of BR remained at between 98.0 - 98.2 %.

Effect of solvent type

Mello et al. [34] investigated the effect of solvent on the reactivity of neodymium versatate/isobutyl aluminum hydride/tert-butylchloride for BD polymerization. Since the solubility parameter (∂) of cyclohexane (16.8) is more similar to that of BD (17.6) than hexane(14.9), the BD polymerization in the presence of cyclohexane was more efficient. It was found that the increase in the amount of cyclohexane in the solvent mixture of cyclohexane/hexane increased the *cis*-1,4 content in BR from 98.2 to 99.1%, whilst the amount of *trans*- 1,4 configuration decreased with a similar *vinyl*-1,2 content of 0.6%. However, the molecular weight of the BR obtained from this catalyst system in the presence of cyclohexane (2.23 x 10^5) was less than that of hexane (3.68 x 10^5), which provided a more favorable chain transfer step than propagation step.

Effect of mixed catalyst system: Nd/Ni

Jang et al. [35] proposed a process for producing high *cis*-1,4 BR by aging a mixture of Nd salt, Ni salt, organoaluminum compound and boron trifluoride complexes. Normally, the Nd salt compounds used for BD polymerization were carboxylate compounds such as neodymium octanoate, neodymium versatate, neodymium hexanoate, neodymium heptanoate or neodymium sterate. Whereas, the nickel salt selected was a nickel carboxylate such as nickel octanoate, nickel naphthenate, nickel stearate or nickel versatate. The boron trifluoride complexes were boron trifluoride-dimethylether, boron trifluride-diethylether, boron trifluoride-dibutylether or boron trifluoride-tetrahydrofuran. The molar ratio of the catalyst mixture (Ni/Nd) was in the range of 1/20 to 20/1, preferably in the molar ratio of 2/8-8/2 and the molar ratio of BF_3/Nd was 0.1/1 to 10/1, preferably in the ratio of 0.5:1-5:1. It was found that a very high *cis*-1,4- content for high yield production could be obtained by using a small amount of catalyst.

Performance of BR with high *cis*-1,4 configuration

Pires et al. [2] reported that the production of high *cis*-1,4 BRs by a Nd-based catalyst which showed a higher stereo-regularity and linearity than the conventional Co and Ni based catalysts. Moreover, the BR produced from the Nd-based catalyst had better resilience and abrasion resistance than that from conventional catalyst systems.

Kwag et al. [36] reported that ultra-high *cis*-1,4 BR produced by monomeric Nd blended with styrene-butadiene rubber (SBR) exhibited high abrasion resistence and a well-balanced anti-wet skid property. For ultra-high cis-1,4 BR blended with natural rubber, low rolling resistance and high abrasion were also obtained.

Moreover, previous literature also reported that the use of Nd in the Ziegler-Natta type catalyst system gave the highest *cis*-1,4 content as presented in Table 1.4. The structure of BR produced from the polymerization catalyzed by the Nd-based catalyst also exhibits higher linearity than that of the conventional catalysts: Co and Ni systems. From both outstanding characteristics, Figure 1.8 shows that there has been more research done on BR obtained from the system catalyzed by a Nd-based catalyst [5].

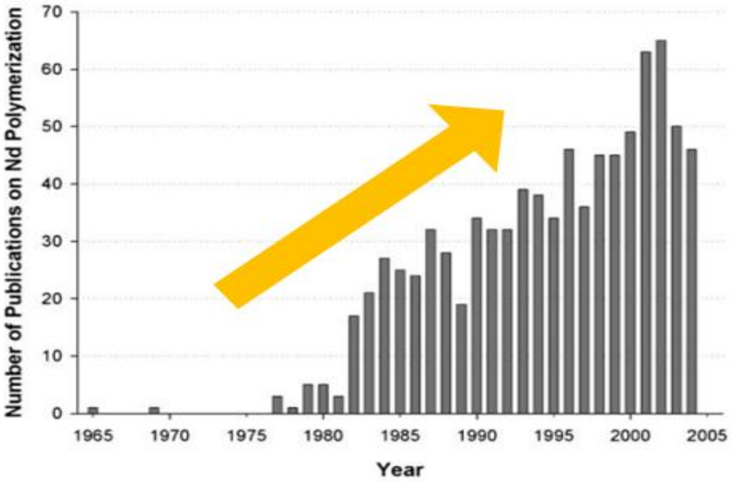


Figure 1.8 Number of publication (scientific papers and patents) in the field of neodymium catalyzed polymerization [5].

However, the disadvantage of the Nd catalyst system is related to its low activity compared to Ni or Co. The price of Nd is also higher than that of the traditional Ziegler-Natta catalysts for butadiene polymerization. Moreover, the BR viscosity is relatively high which is detrimental for acrylonitrile-butadiene-styrene rubber (ABS) production and also induces high cold flow behavior resulting in poor extrudability [37].

Nowadays, commercial butadiene rubbers (BR) are produced via solution polymerization of 1,3-butadiene (BD) catalyzed by using transition metals such as cobalt (Co) or nickel (Ni) coordinated with alkyl metals. The Co-based system consists of cobalt (II) octanoate (Co), diethyl aluminum chloride (DEAC) and water as an activator [24]; while the Ni-based catalyst system is composed of nickel carboxylate (Ni), boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$) and triethyl aluminum

(TEAL) [27, 37]. Both Co and Ni-based catalyst systems produce BR with high *cis*-1,4 configuration (ca. 95% for the Ni-based catalyst and 97% for the Co-based catalyst). It has been observed that a slight increase in the content of *cis*-1,4 configuration greatly improves the elastic properties of BR. Moreover, the high level of *cis*-1,4 units in BR exhibits strain-induced crystallization of raw rubber as well as of the respective vulcanizates [4]. Recently, lanthanide catalysts have been used for producing BR with a high amount of *cis*-1,4 structure. Among the lanthanide metals, neodymium (Nd) is the most active species as presented in Figure 1.9 [4]. Compared to the conventional Co and Ni-based catalyst systems, the Nd-based catalyst provides the highest content of *cis*-1,4 configuration as can be seen in Table 1.5 [14].

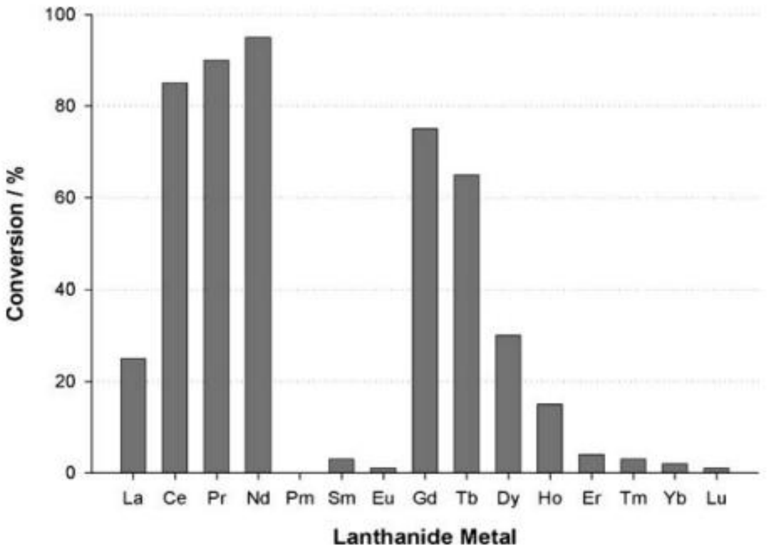


Figure 1.9 Activity profiles of lanthanide metals in catalytic diene polymerization [4].

Table 1.5 Typical composition of BR with different catalyst systems [14].

Catalyst type	Content (%)		
	cis-1,4	*trans*-1,4	*vinyl*-1,2
neodymium	98	1	1
cobalt	96	2	2
nickel	96	3	1
titanium	93	3	4
lithium	36	52	12

Previous literature has also reported that the Nd-based catalyst in the presence of diisobutyl aluminum hydride (DIBAH) and ethyl aluminum sesquichloride (EASC) at n_{DIBAH}/n_{NdV3} of 10 gave BR with the highest content of *cis*-1,4 structure as shown in Table 1.6 and Figure 1.10 [4].

Table 1.6 Technological features of the existing solution processes for high *cis*-1,4 BR production [4].

Items	Co	Ni	Nd
Molar ratio of Al/transition	70-80/1	40/1	10-15/1
Co-catalyst & chlorinating agents	DEAC	TEAL, $BF_3 \cdot Et_2O$	DIBAH, EASC
Cis-1,4 content	96%	97%	98%
Linearlity of BR	adjustable	branched	highly linear

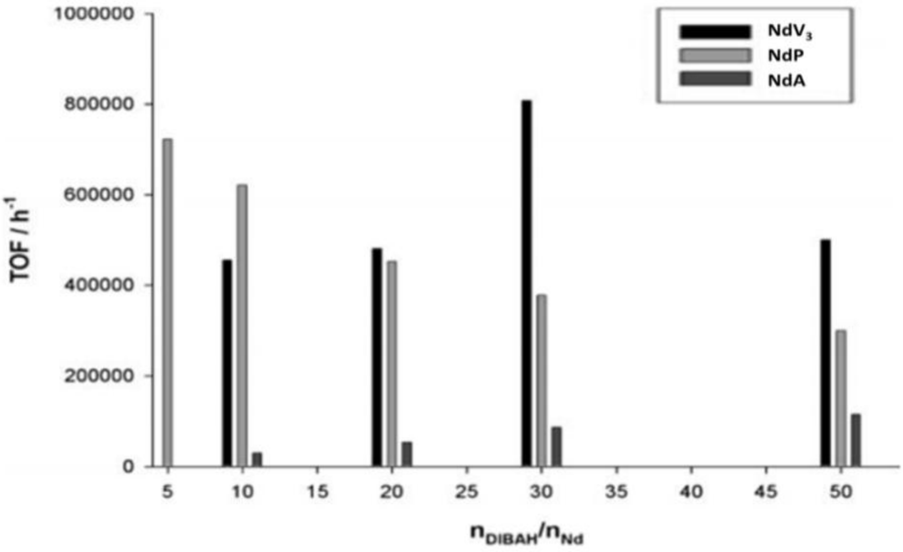


Figure 1.10 Turnover number of frequency (TOF) of various types of Nd precursor for BD polymerization [4].

1.5 Objective and Scope of Dissertation

It is well known that high *cis*-1,4 BR is produced by the polymerization of BD using Ziegler-Natta catalysts consisting of transition metals such as Ni, Co or lanthanide and co-catalysts such as the alkyl aluminum compounds. In industry, triethylaluminum (TEAL) and diethylaluminum (DEAC) are normally used as the co-catalysts for Ni- and Co-based catalyst systems, respectively. For the production of

BR containing high *cis*-1,4 structure content with good physical and mechanical properties by using catalysts of reasonable cost for the commercial market, the main objective of this research was to study the BD polymerization reaction by using Co/Nd- and Ni/Nd-based Ziegler-Natta catalysts. The effect of reaction parameters such as molar ratios of Co/Nd and Ni/Nd, amount of co-catalysts, solvent type and reaction temperature on yields and characteristics of the obtained BR were investigated. The physical and thermal properties of the obtained BR and its vulcanizates were also compared to the commercial ones.

In Chapter I, the BR chemistry, technology, applications and type of catalyst used for producing BR are described.

In Chapter II, the experiment procedures for polymerization of BD as well as the compounding recipe are presented. The various techniques used for the characterization of the BRs obtained are also given.

In Chapter III, a preliminary study of BD polymerization using Nd-based catalyst system is described.

In Chapter IV, the effects of reaction parameters such as Co/Nd molar ratio, polymerization temperature, monomer concentration, co-catalyst loading and type of solvent used for BD polymerization when using a Co/Nd-based catalyst in terms of %conversion and physical properties of the obtained BR are reported. The mechanical properties of the BR vulcanizates are also compared with commercial BRs.

In Chapter V, the BD polymerization catalyzed by using a Ni/Nd-based catalyst is presented. The effects of Ni/Nd molar ratio, polymerization temperature, monomer concentration and type of solvent on the level of BD conversion and the physical properties of the BR obtained as well as mechanical properties of the BR vulcanizates compared with the commercial ones are reported.

In Chapter VI, conclusions based on the results obtained from this research and recommendations for future works are summarized.

CHAPTER II

EXPERIMENTAL AND CHARACTERIZATION

2.1 Materials

2.1.1 BD polymerization using Nd- and Co/Nd-based Ziegler-Natta catalyst system

1,3-Butadiene (BD, 96% purity), methanol (99.9% purity) and a solution mixture containing 2.0% (w/w) cobalt octoate (Co), 15% (w/w) diethylaluminum (DEAC) and 2.0% (w/w) triethylaluminum (TEAL) in the presence of toluene were supplied by BST Elastomer Co., Ltd. (Rayong, Thailand). The amount of water in toluene was controlled at <10 ppm by purging with nitrogen gas (99.99% purity) before charging into the polymerization unit. Neodymium versatate (NdV_3) dissolved in cyclohexane (8.8% (w/v) was purchased from Comar Petrochemical Co., Ltd. (Cape Town, South Africa). It was diluted to 1.0 % (w/v) in oxygen free-toluene before charging into the polymerization reactor. 2,6-di-tert-butyl-4-methyphenol (BMP) and phosphate of polyoxyethylene alkyl phenyl ether (PPA) were purchased from Lanxess Deutschland GbmH (Germany) and Twin Hart International Co., Ltd. (Taiwan), respectively. A 5.6% (w/w) of BMP/PPA solution mixture (10/3 (w/w)) was prepared by dissolving in toluene.

2.1.2 BD polymerization using Ni/Nd-based Ziegler-Natta catalyst system

BD (95% purity) was purchased from Air liquid Co.,Ltd. BD and purified by passing through a TEAL solution as shown in Figure 2.1. Nickel naphthenate (Ni) (2.0% (w/w) in hexane), DEAC (1 M in hexane), TEAL (1 M in hexane), methanol and toluene (99 % purity) were purchased from Sigma Aldrich. Toluene was purified by distillation and the amount of water in the distilled toluene was controlled (< 10 ppm) by using molecular sieve 4A and purging with nitrogen gas (99.99% purity) before using in the polymerization unit. 8.8% (w/v) NdV_3 in the presence of cyclohexane obtained from Comar Petrochemical (Cape Town, South Africa) was diluted to 1.0% (w/v) using dry toluene before charging into the polymerization reactor.

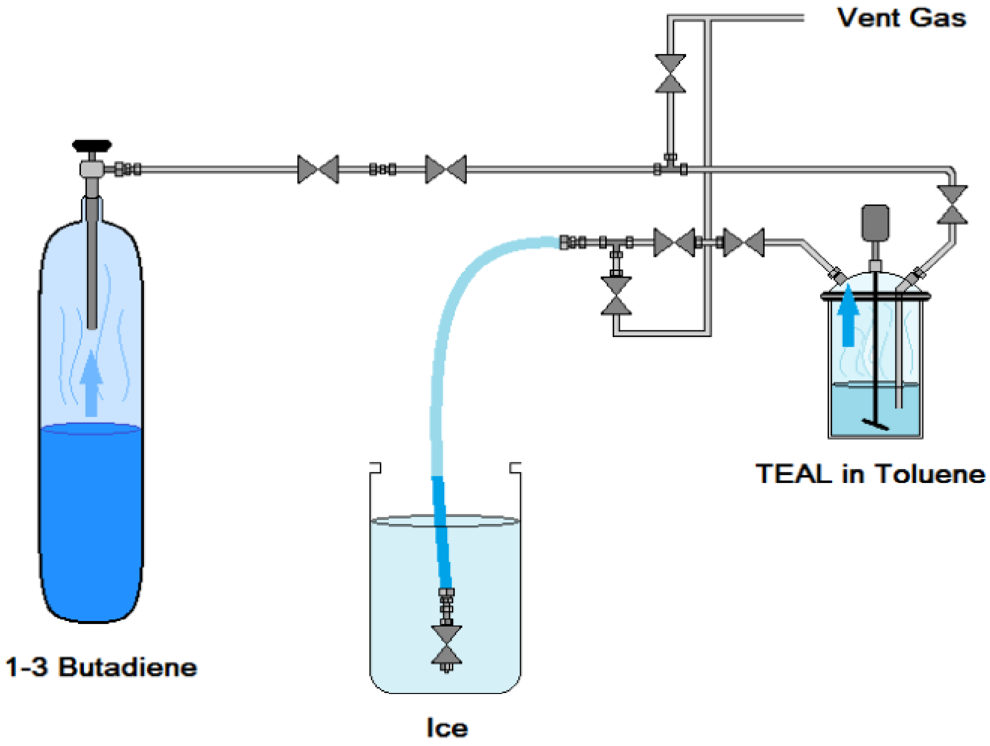


Figure 2.1 Purification unit of BD monomer.

2.1.3 Commercial butadiene rubbers (BR)

Commercial butadiene rubber (Nd-BR) obtained from the conventional BD polymerization catalyzed by using Nd-based catalyst Ziegler-Natta catalyst system was purchased from Lanxess Co., Ltd. (Germany). Commercial BR obtained from Ni- and Co-based Ziegler-Natta catalyst systems, Ni-BR and Co-BR, respectively were provided by BST Elastomers Co., Ltd. (Thailand), respectively. The physical properties of these BRs are summarized in Appendix A (Table A-1)

2.1.4 Chemicals for BR vulcanization

Sulfur (Tsurumi chemical industry, Japan), stearic acid (Kao Corporation, Japan), zinc oxide (ZnO, Sakai chemical industry, Japan), n-tert-butyl-benzothiazole sulfonamide (TBBS, Monflex PTE Ltd), sun oil (Sunoco, Japan) and carbon black IRB No. 7 (USA) were used as received for BR vulcanization.

2.2 Catalyst Preparation

2.2.1 NdV_3-based Ziegler-Natta catalyst

The NdV_3 catalyst solution was prepared by transferring 1.0% (w/v) of NdV_3 to 100 mL ampoule following the fill of DEAC and TEAL (DEAC/Nd molar ratio = 0.8 – 3.2 and TEAL/Nd molar ratio = 4.0 – 7.0). Before charging into a 500 mL glass bottle for starting the BD polymerization, the catalyst solution was aged in a water bath at 20 °C for 1 h.

2.2.2 Co/Nd based Ziegler-Natta catalyst

The NdV_3 solution (1.0% (w/v)) was mixed with the desired amounts of Co, DEAC and TEAL in a degassed dried – glass ampoule capped with a neoprene rubber septum. The Co/Nd molar ratio was varied from 0.0/1.0 to 1.0/0.0 with 0.5 – 2.0 and 3.0 – 9.5 of DEAC/Nd and TEAL/Nd molar ratios, respectively. The catalyst solution was then aged in a water bath at 20 ^{o}C for 1 h before charging into the polymerization reactor.

2.2.3 Ni/Nd based Ziegler-Natta catalyst

The Ni/Nd catalyst solution was prepared in a degassed dry-glass ampoule capped with a neoprene rubber. The NdV_3 solution (1.0% (w/v)) was mixed with Ni, DEAC and TEAL in the following molar ratios: Ni/Nd molar ratio = 0/1 to 1/0, DEAC/Nd molar ratio = 0.5/1.0 – 3.0/1.0 and TEAL/Nd molar ratio = 3.0/1.0 – 9.0/1.0. The obtained catalyst solution was then aged in a water bath at 20 ^{o}C for 1 h before charging into the polymerization reactor.

2.3 BD Polymerization

2.3.1 Preliminary study for BD polymerization using NdV_3 catalyst

The screening test for preliminary study of BD polymerization using NdV_3 catalyst diluted to 1.0 % (w/v) in oxygen free-toluene was performed in 500 mL-glass bottles. First, charging BD at the desired content into a 500 mL glass bottle containing toluene (toluene/BD = 4 (w/w)) following the injection of the aged catalyst (2.6 mL). The BD polymerization was carried out at 50 °C and allowed to proceed for 2 h. When the reaction was terminated, the BR syrup was coagulated in methanol and then dried in an oven at 80°C. The BR obtained from the Nd/DEAC/TEAL was shown in Figure 2.2. The flow diagram of preliminary experiments was shown as Figure 2.3.

Figure 2.2 BR products after drying at 80 °C.

Figure 2.3 Flow diagram of screening test for BD polymerization.

2.3.2 BD polymerization using Co/Nd catalyst

All solution polymerization systems were carried out in a 1- and 2-Liter Parr reactor under a dry nitrogen atmosphere. First, the dry toluene was charged into the reactor. Then, the aged catalyst of the Co/Nd-based catalyst (5.4 mL) was injected into the reactor using a syringe and the reactor was heated to reach the desired temperature (45 – 60 °C). Then, 80 g of BD was charged into the reactor. After 2 h. of reaction time, the polymerization was terminated by adding 12 mL BMP/PPA solution. The obtained polymeric syrup was then coagulated in methanol under stirring to obtain the BR crumb. The resulting BR product was dried in an oven at 80 °C for 2 h.

2.3.3 BD polymerization using Ni/Nd catalyst

All solution polymerizations were carried out in a 0.5 Liter Parr reactor. The reaction process system was maintained under a dry nitrogen atmosphere. First, dried toluene was charged into the reactor. Then, 1.1 mL of aged catalyst solution was injected using a syringe when the desired temperature of the reactor was reached (45-60 °C), followed by the charging of 15 g of BD into the reactor. The polymerization was terminated by adding 3 mL of BMP/TNP solution after polymerization proceeded for 2 h. The polymer cement was coagulated using methanol under stirring to obtain the BR crumb. The resulting BR product was dried overnight.

The %conversion of 1,3-BD was calculated using Eq. 2.1:

$$\%\text{Conversion} = \frac{\text{TSC}}{\text{M}} \times 100 \qquad (2.1)$$

where TSC is the total solid content (g) and M is the weight of the charged 1,3-BD monomer (g). All steps for the BD polymerization are shown in Figure 2.4

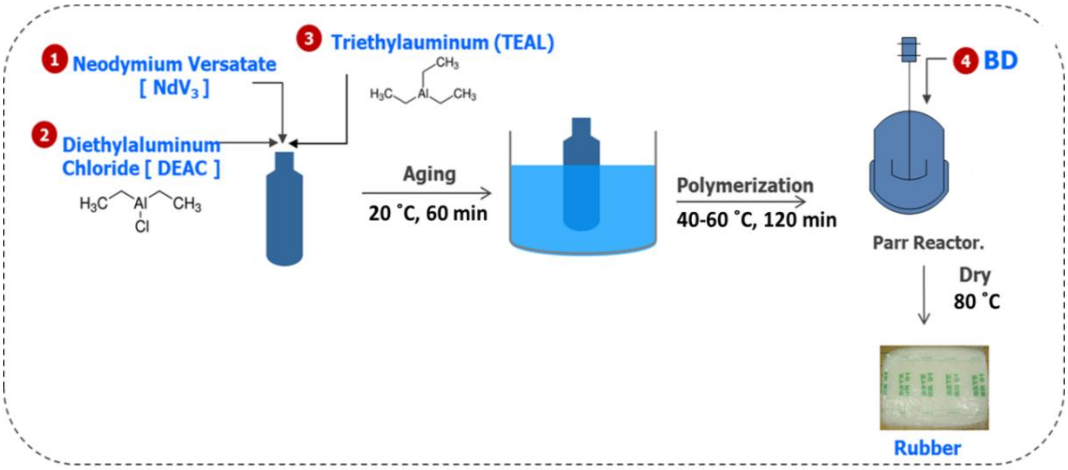


Figure 2.4 Scheme of BD polymerization.

2.4 Vulcanization Process for BR

The vulcanization characteristics and mechanical properties of BR vulcanizates obtained from BD polymerization using the Co/Nd-based catalyst (Co/Nd-BR) and Ni/Nd-based catalyst (Ni/Nd-BR) were compared with commercial Co-BR, Ni-BR and Nd-BR.

Co/Nd-BR, the commercial Co-BR and Nd-BR (400 g) were each compounded with zinc oxide (ZnO, 3 parts per hundred of rubber (phr)), stearic acid (2 phr), sulfur (1.5 phr), TBBS (0.9 phr), sun oil (15 phr) and carbon black (60 phr) by using an internal mixer at 30 ºC with a rotor speed of 50 rpm. Then the compounded BR was sheeted by using a 2-roll mill at 40 °C in order to increase homogeneity and eliminate air bubbles inside the rubber sheets. After they were left at room temperature overnight, they were vulcanized in an electrically heated compression mould at 145°C for 35 min.

In the case of Ni/Nd-BR, its vulcanization characteristics and mechanical properties were compared with commercial BRs: Ni-BR and Nd-BR. 80 g Ni-BR or Nd-BR was mixed with the vulcanizing agents with similar amounts as described above by using an internal mixer at 70 °C with a rotor speed of 40 rpm followed by sheeting with the two-roll mill at 50 ^{o}C. After the rubber compounded sheets were left at room temperature overnight, they were vulcanized in the electrically heated compression mould at 145 °C for 35 min.

2.5 Structural Characterization

The chemical structures of the Co/Nd-BR and Ni/Nd-BR were analyzed by using an attenuated total reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR, Perkin Elmer FT-IR spectrometer, Paragon 500) and nuclear magnetic resonance spectroscopy (NMR, Avance Bruker 500 MHz spectrometer).

For ATR-FTIR spectroscopy, the sample was placed on the top of an ATR crystal and then the spectrum was recorded with 4 scans at 25 ºC. The contents of *cis*-1,4, *trans*-1,4 and *vinyl*-1,2 configurations were calculated using Eqs. 2.2 – 2.4 according to ISO 12965:2000(E) using the normalized peak height of the band absorbance at 738 (A_{738}), 910 (A_{910}) and 964 (A_{964}) cm^{-1} for *cis*-, *vinyl*- and *trans*-R-CH=CR-H, respectively.

$$\%cis = \frac{A_{738}}{A_{738}+A_{910}+A_{964}} \times 100 \qquad (2.2)$$

$$\%vinyl = \frac{A_{910}}{A_{738}+A_{910}+A_{964}} \times 100 \qquad (2.3)$$

$$\%trans = \frac{A_{964}}{A_{738}+A_{910}+A_{964}} \times 100 \qquad (2.4)$$

Proton nuclear magnetic (^{1}H-NMR) and carbon nuclear magnetic (^{13}C-NMR) spectroscopy were used to confirm the microstructures of BR. 0.01 g of rubber sample was dissolved in chloroform-*d* ($CDCl_3$) at room temperature and the spectra were recorded with 16 and 10,000 scans respectively with trimethylsilane (TMS) as an internal standard. The amounts of all configurations calculated by using the peak areas obtained from ^{1}H-NMR and ^{13}C-NMR spectra were also shown in Appendix B (Table B-1 and Table B-2).

2.6 Glass Transition Temperature of BR

The glass transition temperature (T_g) of Co/Nd-BR, Co-BR and Nd-BR was determined by using a dynamic mechanical analyzer (DMA, GABO/Eplexor) following ASTM 5279 with a tension mode under a nitrogen atmosphere. The sample was prepared with a thickness of 1.75 mm and a width of 10 mm. The heating rate was controlled at 20 ºC/min with 1 Hz of applied frequency. The testing temperature was over the range of -150 to 60 ºC. The T_g value for each sample was calculated from the maximum peak of the base-line shift of the DMA thermogram.

For the T_g evaluation of Ni/Nd-BR, Ni-BR and Nd-BR; they were analyzed by using Differential Scanning Calorimetry (DSC, Shimadzu DSC-50). The instrument signal was derived from the temperature difference between the sample and the reference. 10 mg of sample was scanned as the temperature changed from -130 ºC to 50 ºC at a heating rate of 5 ºC/min. The T_g value of each sample was calculated from the midpoint of the base-line shift of the DSC thermogram.

2.7 Measurement of Gel Content

The gel content in the BR samples was measured by putting a 0.3 g rubber sampleinto a container made from a metal screen sheet (80 mesh). Then, it was immersed in 100 mL of toluene for 24 h. The rest of the sample in the container was dried in a vacuum oven at 60 ºC for 2 h. The gel content was calculated according to Eq. 2.5.

$$\%\text{gel content} = \frac{\text{Final sample weight}}{\text{Initial sample weight}} \times 100 \qquad (2.5)$$

2.8 Molecular Weight and Molecular Weight Distribution of BR

The molecular weight (Mw) and molecular weight distribution (MWD) of the prepared BRs were determined by using a gel permeation chromatography (GPC, Waters 2690) equipped with a refractive index detector (Waters 2410). The mobile phase was tetrahydrofuran (THF) at a flow rate of 1 mL/min and controlled at 25 ^{o}C. BR samples dissolved in THF at 0.1% (w/v) were injected into the GPC. A universal calibration curve was prepared by using mono-dispersed polystyrene standards. The MWD was also determined using the polydispersity index (PDI) which was equal to Mw/Mn.

2.9 Cure Characteristics of BR

The cure characteristics of the compounded BRs were analyzed by using a moving die rheometer (MDR 2000, Alpha Technologies) at 160 ^{o}C for 30 min to obtain the minimum (M_L) and maximum torques (M_H) with scorch time (ts_1) and optimum cure time (tc_{90}) according to ASTM D5289-07.

2.10 Mooney Viscosity (ML1+4)

The Mooney viscosity of the compounded BRs was measured by using a Mooney viscometer (Shimazu viscometer, Model SMV 202) at 100 ºC following ASTM D1646.

2.11 Mechanical Properties of BR Vulcanizates

Tensile properties

The tensile properties of the vulcanized BRs were investigated by using a tensile tester (Instron 5565A) with a crosshead speed of 500 mm/min following ASTM D412-06.

Rebound resilience

The repulsive elasticity properties of the vulcanized BRs were evaluated. Its resilience was determined by using a Lupke rebound resilience tester (VR-6510, Ueshima Seisakusho) following JIS K 6255.

Abrasion tester

The abrasion resistance of vulcanized BRs was evaluated according to DIN 53516 using a DIN abrasion tester (ZWICK, USA).

Heat build-up

The heat build-up of the vulcanized BRs was measured using a BF Goodrich Flexometer (Model II) following ASTM D623.

Hardness

The measurement of hardness of the vulcanized BRs was carried out according to ASTM 2240nusing the Shore A hardness tester (WALLACE).

CHAPTER III

PRELIMINARY STUDY OF 1,3-BUTADIENE POLYMERIZATION USING Nd- AND Co/Nd-BASED ZIEGLER-NATTA CATALYSTS

Although the Nd-based catalyst produces BR with a high content of *cis*-1,4 configuration resulting in superior characteristics which can be applied in various applications, the price of Nd is higher than that of the traditional Ziegler-Natta catalyst for BD polymerization and it is also dependent on China's economics, since China is the largest Nd producer. To consider the general BR processes using the Co- or Ni-based Ziegler-Natta based catalyst, the co-catalysts, DEAC and TEAL, are required and their prices are major factor. Moreover, careful handling is required due to safety aspects.

As a concern about the technology for producing the high performance BR with practical economics and safety, the BD polymerization using Nd coordinated with the general co-catalysts such as DEAC and TEAL was investigated. Before reporting on the systematic study, some preliminary experiments were performed to determine the initial amounts of catalyst and co-catalyst required including the conditions for BD polymerization.

3.1 Color of NdV_3/DEAC/TEAL Catalyst Solution

When 1.0% (w/v) NdV_3 dissolved in toluene was mixed with 15.0% (w/w) DEAC and 2.0% (w/w) TEAL in the presence of toluene at DEAC/Nd and TEAL/Nd molar ratios of 1.6 and 5.1, respectively in a degassed dried-glass ampoule capped with a neoprene rubber septum, the color of NdV_3 solution changed from reddish purple to green as can be seen in Figure 3.1. It is possible that DEAC and TEAL acting as the Lewis acids changed the ionic characteristics of Nd from Nd^{3+} (reddish purple) to Nd^{2+} (green color) indicating the formation of the active catalytic species [38, 39]. This similar color change was also reported in a previous patent [40].

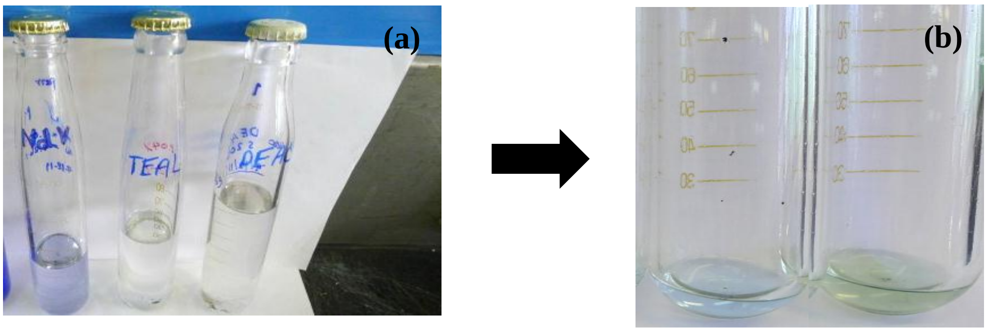


Figure 3.1 Color of (a) NdV_3, TEAL and DEAC solutions and (b)NdV_3/DEAC/TEAL solution with a molar ratio of 1.0/1.6/5.1.

3.2 Color of (Co/Nd)/DEAC/TEAL Catalyst Solution

When the (Co/Nd) catalyst at a molar ratio of 0.1/1.0 to 0.4/0.6 in the presence of toluene mixed with 15.0% DEAC and 2.0% TEAL was dissolved in toluene at the DEAC/Nd and TEAL/Nd molar ratios of 1.6 and 5.1, respectively, the color of the obtained catalyst solution changed from reddish purple for the NdV_3 solution and dark blue for the Co solution to dark yellow as shown in Figure 3.2. Since the DEAC and TEAL were considered to act as Lewis acids, this phenomenon has been found for the combination of cobalt halides with Lewis acids such as ethyl aluminum dichloride and sesquihalide [41].

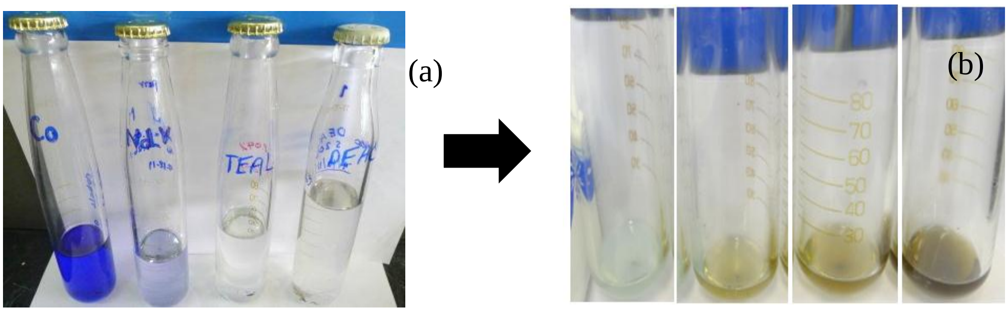


Figure 3.2 Color of (a) Co, NdV_3, TEAL and DEAC solutions and (b) (Co/Nd)/DEAC/TEAL solution at a molar ratio of (0.1/1.0 – 0.4/0.6)/1.6/5.1.

3.3 BD Polymerization Catalyzed by NdV_3/DEAC/TEAL

Without the use of TEAL acting as an alkylation agent, the results in Table 3.1 showed that the BD polymerization was not activated and no rubber was formed in the bottle (Figure 3.5). It was also noticed that an increase in the molar ratio of DEAC/Nd from 0.8 and 1.6 increased the level of BD conversion from 73.6% to 93.6% when the TEAL/Nd molar ratio was kept constant at 7.0. This could be explained in that the chloride of DEAC was transferred to Nd to form the active catalytic species [4].

For the effect of TEAL concentration (Table 3.1), it was observed that an increase in the TEAL/Nd molar ratio from 4.0 to 7.0 increased the BD conversion from 90.9% to 93.6% at a molar ratio of 1.6. This indicated that the increase in the amount of TEAL was more effective for BD polymerization due to the effect of TEAL, which acted as a scavenger for moisture and oxygen possibly present in the process [4, 41]. In addition, TEAL was the Lewis acid, which could abstract halides or alkyl groups from Nd to create the active sites [4, 41]. From the preliminary results in Table 3.1, it was found that the maximum BD conversion (95.9%) was achieved when the DEAC/Nd and TEAL/Nd molar ratios of 1.6 and 5.1, respectively were applied.

Table 3.1 Effect of DEAC and TEAL concentration on %conversion of BD polymerization catalyzed by using NdV_3/DEAC/TEAL.

DEAC/Nd	TEAL/Nd	% Conversion
0.8	0	0
1.6	0	0
3.2	0	0
0.8	4.0	14.0
0.8	5.1	44.3
0.8	6.0	55.1
0.8	6.5	65.1
0.8	7.0	73.6
1.6	4.0	90.9
1.6	5.1	95.9
1.6	6.5	94.3
1.6	7.0	93.6

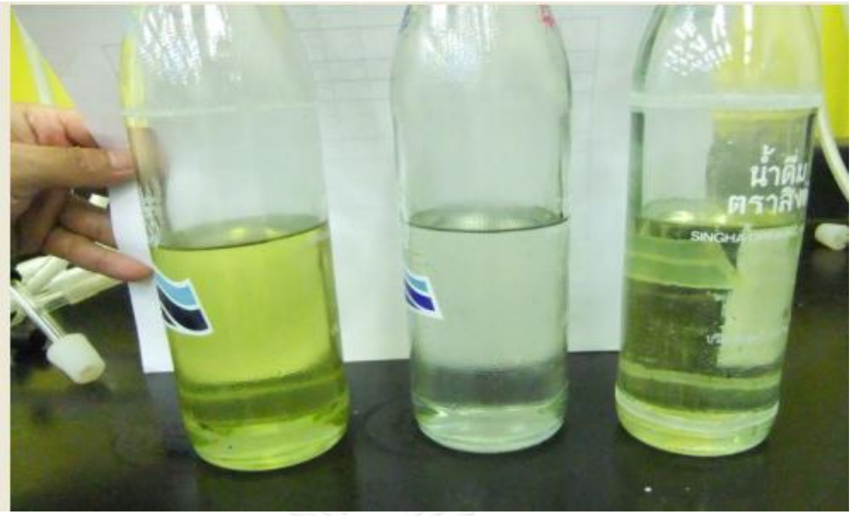


Figure 3.3 No reaction occurred in the BD polymerization using NdV_3/DEAC.

3.4 BD Polymerization Catalyzed by (Co/Nd)/DEAC/TEAL

A screening test for BD polymerization was performed in a 500 mL glass bottle containing 1.0% (w/v) of NdV_3 dissolved in toluene mixed with 2.0% (w/w) Co, 15% (w/w) DEAC and 2.0% (w/w) TEAL in the presence of toluene in a degassed dried glass ampoule and capped with neoprene rubber. The Co/Nd molar ratio was varied from 0.0 to 0.4 coordinated with 1.6 and 4.0 – 5.6 of DEAC/Nd and TEAL/Nd molar ratios, respectively. After aging in a water bath at 20 °C for 1 h, the polymerization was carried out at 50 °C for 2 h.

When the molar ratios of DEAC/Nd and TEAL/Nd were kept constant at 1.6 and 5.1, respectively, it was found that the increase in the molar ratio of Co/Nd from 0.1 to 0.4 yielded the BD conversion higher than 90% (Table 3.2). The obtained BR also had a high content of *cis*-1,4 configuration at 94 – 95% conversion. This indicated that this mixed Co/Nd mixed catalyst had high potential to produce BR as well as the conventional BD polymerization using Co- and Nd- based catalyst systems.

Table 3.2 Mixed catalyst (Co/Nd) molar ratio on % conversion and % *cis*-1,4 content.

Co/Nd	TEAL/Nd	% Conversion	% *cis*-1,4
0.0	5.1	91.5	94.0
0.1	5.1	93.7	94.4
0.2	5.1	94.1	95.2
0.4	4.0	no reaction	0
0.4	5.1	81.1	97.1
0.4	5.6	85.4	96.7

DEAC/Nd molar ratio = 1.6

CHAPTER IV

POLYMERIZATION OF 1,3-BUTADIENE USING Co/Nd-BASED ZIEGLER/NATTA CATALYST: MICROSTRUCTURE AND PHYSICAL PROPERTIES

For the Co-based catalyst system, it consists of cobalt (II) octanoate, diethyl aluminum chloride (DEAC) and water as an activator [23, 24] . This system provides Co-based BR with a high branching level and low solution viscosity, making it appropriate for the production of acrylonitrile-butadiene-styrene (ABS) and high impact polystyrene (HIPS) [4, 8]. Moreover, the high content of branching can decrease the cold flow effect of uncured BR to provide an advantage for preparation of compounded rubbers and rubber solutions [2, 4]. However, the drawback of the Co-BR arises from crosslinking resulting in gel formation which greatly affects the processing behavior and surface appearance of the extruded products [23]. It also has a long optimum cure time (t_{90}) and low tackiness [2]. Moreover, the low solubility of the applied water as the activator for Co/DEAC in solution polymerization induces instability in the process [23].

Among the Ziegler-Natta catalysts for producing BR, a Nd-based catalyst exhibits the best performance to produce the highest amount of *cis*-1,4- configuration (ca. > 98%) with very low content of *vinyl*-1,2 structure (< 1%). The high *cis*-1,4 structure content gives rise to a BR having the lowest glass transition temperature (T_g) (ca. -110^{o}C) [4, 36] which is suitable for application in very low temperature situations. It also provides strain-induced crystallization properties to promote better green strength with a highly effective tackiness compared to other rubbers in the blends [2, 36, 42]. In addition, Nd-based BR has lower heat build-up, higher linearity providing better elasticity and resilience properties and greater abrasion resistance [4, 8]. This excellent abrasion resistance is shown in Figure 4.1 [43]. However, the relatively high viscosity and molecular weight of the Nd-BR is inappropriate for ABS production. Its high linearity also promotes high cold flow behavior resulting in poor extrudability [4]. Moreover, the molecular weight of Nd-BR is difficult to control [4].

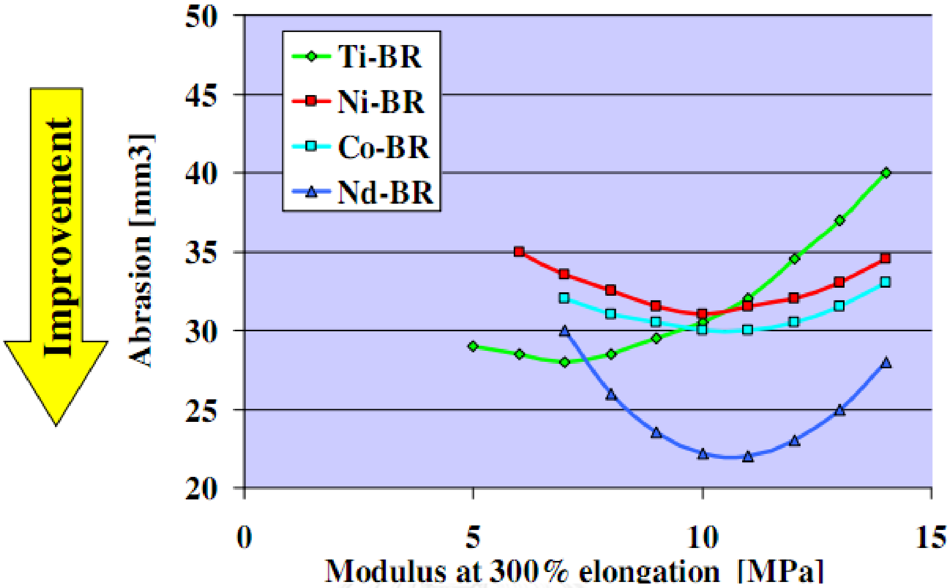


Figure 4.1 1,4-*cis* BR: Abrasion Resistance of BR-Vulcanizates (DIN-Abrasion).

To balance the advantages of the Co- and Nd-based catalyst systems, this research aimed at a study of the polymerization of 1,3-butadiene (BD) catalyzed by using a mixed catalyst containing Co and Nd (Co/Nd) with DEAC and TEAL used as co-catalysts. The effects of the Co/Nd molar ratio, TEAL content, DEAC concentration, BD concentration, reaction temperature and solvent type on %conversion, microstructure, molecular weight (Mw) and molecular weight distribution (MWD) of the resulting BR gum (Co/Nd-BR) were examined. The apparent activation energy of this process was also evaluated. Moreover, the vulcanization and mechanical properties of the Co/Nd-BR vulcanizates were investigated and compared to commercial BRs obtained from the Co- and Nd-based polymerization processes.

4.1 Chemical Structure, Tg and Gel Content of Co/Nd-BR.

In the presence of toluene, the chemical structure of Co/Nd-BR obtained from the polymerization of 3.01 M of [BD] carried out by using a 0.4/0.6 Co/Nd molar ratio of 1.5 and 5.0 for DEAC/Nd and TEAL/Nd molar ratios, respectively at 50°C for 2 h was analyzed by using ATR-FTIR spectroscopy (Figure 4.2) and compared to those of commercial BRs: Co-BR and Nd-BR. The amount of each configuration in the chemical structure of all BRs is presented in Table 4.1.

Table 4.1 Microstructure, T_g and gel content of BRs.

BR	Microstructure (%)			T_g	Gel content
	Cis-1,4	*Trans*-1,4	*Vinyl*-1,2	(ºC)	(%)
Co-BR	98.0	0.81	1.19	-100	0.04
Nd-BR	97.6	2.12	0.28	-98	0
(Co/Nd)-BR*	98.2	1.40	0.40	-102	0

*Condition: [BD] = 3.01M, Co/Nd molar ratio = 0.4/0.6, TEAL/Nd molar ratio = 5.0, DEAC/Nd molar ratio = 1.5 at 50 ºC for 2 h in toluene

Figure 4.2 shows that the Co/Nd-BR structure had high intensity of the transmittance peak at 738 cm^{-1} indicating a high level of *cis*-1,4 configuration (ca. 98%). This implied that the Co/Nd mixed catalyst had similar potential to Co- and Nd-based catalyst systems to produce BR with a high level of *cis*-1,4 structure. However, the Co/Nd-BR obviously exhibited a very low intensity of the transmittance signal attributed to the *vinyl*-1,2 configuration at 910 cm^{-1}. The results in Table 4.1 showed that the Co/Nd-BR had only 0.77% *vinyl*-1,2 structure, which was lower than that of Co-BR (1.19%). This indicated that the Co/Nd mixed catalyst had greater selectivity to produce BR with a high *cis*-1,4 structure and a low amount of *vinyl*-1,2 configuration. This was mainly due to the influence of Nd in the mixed catalyst to provide a faster BD polymerization to form an external σ-allyl species than the internal ones, which allowed less opportunity to generate the *vinyl*-1,2 structure in BR [44]. In addition, the steric and electronic nature of the various catalysts are also an important factor to form the 1,4- or 1,2-configurations of the obtained polymers as shown in Figure 4.3 [3].

Furthermore, it was also observed that the existence of Co in the mixed catalyst induced Co/Nd-BR to provide a lower *trans*-1,4 configuration (1.33%) than the Nd-BR (2.12%). Thus, the lower amounts of both *vinyl*-1,2 and *trans*-1,4 units in the Co/Nd-BR than that of Co-BR and Nd-BR, respectively were expected to promote easier crystallization under tension [2].

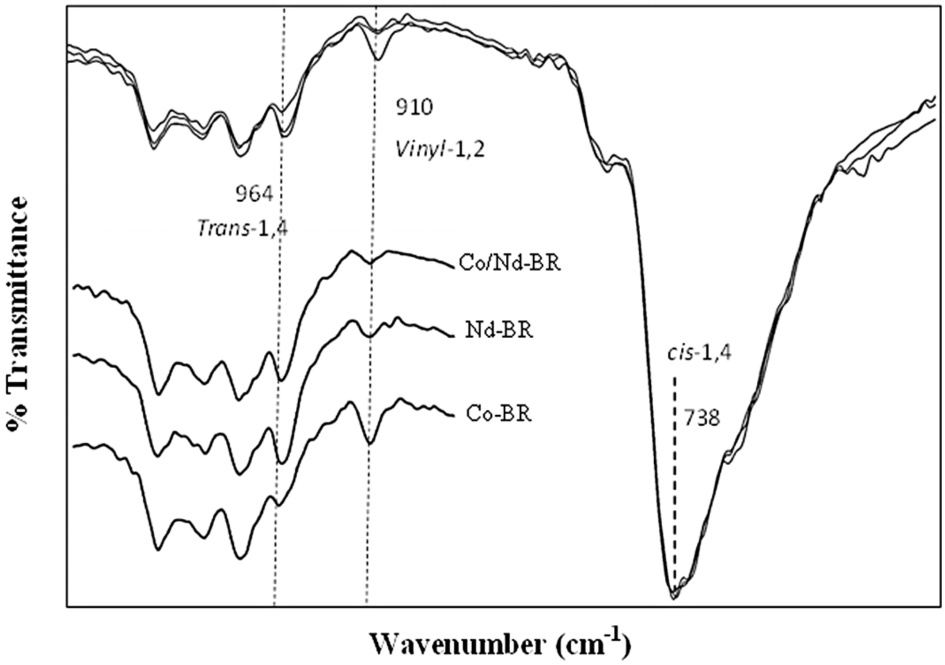


Figure 4.2 Comparative ATR-FTIR spectra of Co/Nd-BR and commercial BRs:Nd-BR and Co- BR.

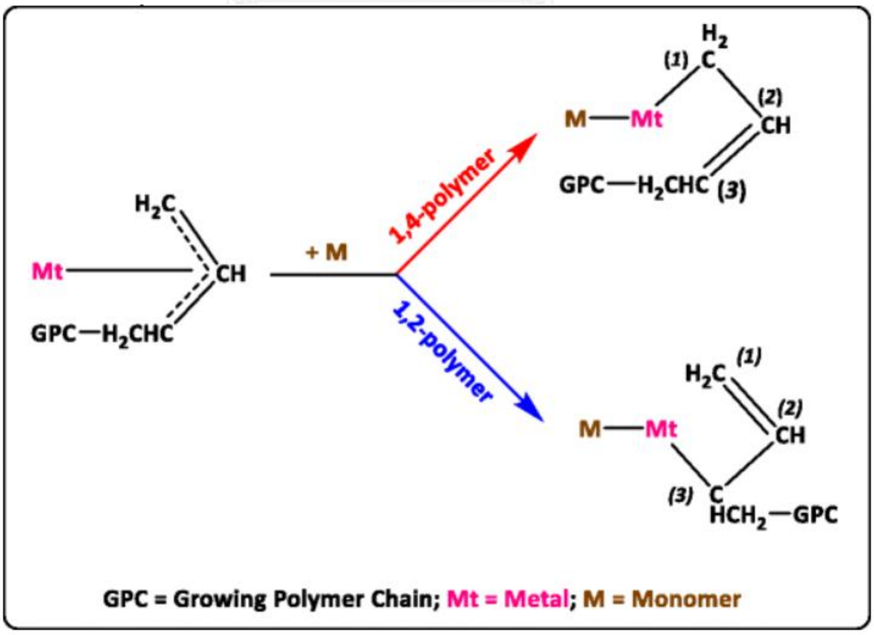


Figure 4.3 Pathway of chemo-selective 1,4- and 1,2-polymer formation [3].

The microstructure of Co/Nd-BR was also comparatively determined by means of ^{1}H-NMR and ^{13}C-NMR spectroscopy. The ^{1}H-NMR spectra of all BR sample (Figure 4.4a) showed the signals at a chemical shift (δ) of 4.8 – 5.2 ppm for $=CH_2$ of *vinyl*-1,2 configurations and 5.2 – 5.8 ppm for –CH= of 1,4-BD and 1,2-BD units [45, 46]. It was found that Nd-BR and Co/Nd-BR exhibited lower signals for the $=CH_2$ of *vinyl*-1,2 structure than Co-BR. For ^{13}C-NMR spectroscopy, Figure 4.4b shows the important ^{13}C-NMR signals of chemical shifts at 27.4, 32.7 and 34.0 ppm which are attributed to the 1,4-*cis*-methylene, $-CH_2-$ of 1,4-*trans* structure and vinyl-1,2-enchainment, respectively [47]. This observation was also consistent with the result from ^{1}H-NMR spectroscopy which exhibited a very low signal intensity of *vinyl*-1,2 configuration of Co/Nd-BR.

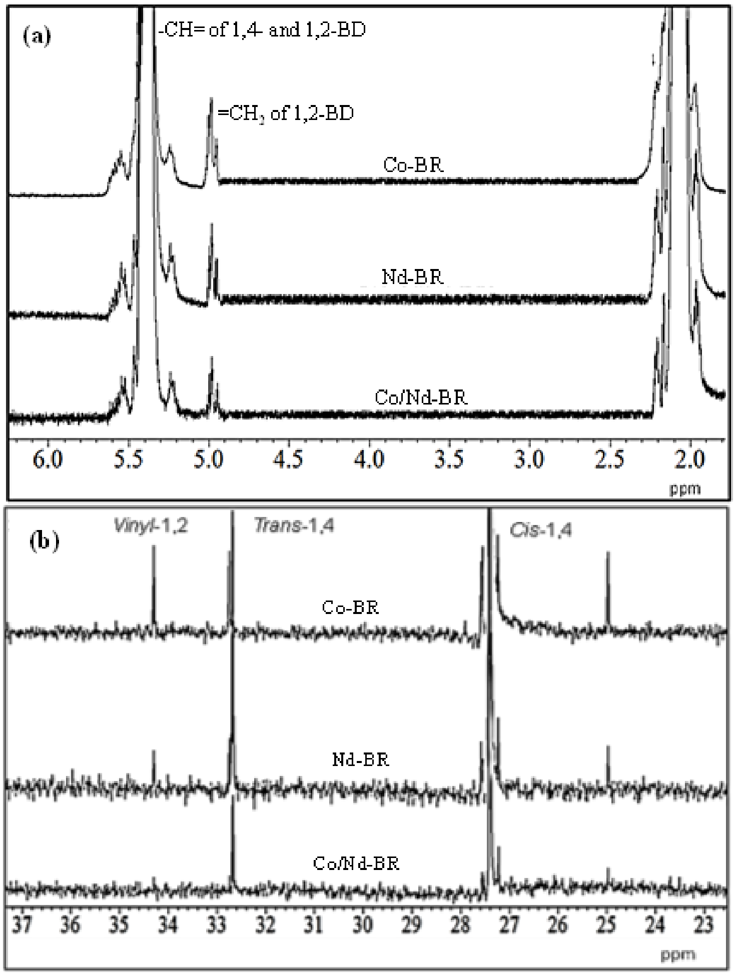


Figure 4.4 Chemical structure of BRs: (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of Co/Nd-BR,Nd-BR and Co-BR.

To evaluate the T_g value and gel content of Co/Nd-BR and compare it with commercial Nd-BR and Co-BR, the results in Table 4.1 show that Co/Nd-BR had the lowest T_g at -102°C, whereas the T_g values of Co-BR and Nd-BR were -100 and -98°C, respectively. This was due to the high portion of *cis*-1,4-configulation with very low *vinyl*-1,2 configuration of the Co/Nd-BR. Moreover, Co/Nd-BR and Nd-BR with a very low amount of *vinyl*-1,2 configuration did not incur any gel formation. Whereas the commercial Co-BR containing a higher content of *vinyl*-1,2 structure had a gel content of ca. 0.04%. It is likely that the existing *vinyl*-1,2 configuration could easily induce the gel formation in BR via re-incorporation of internal unsaturation units for the Co-BR [8, 48].

4.2 BD Polymerization Using Co/Nd-Based Ziegler/Natta Catalyst

The effect of reaction parameters on BD polymerization using the Co/Nd-Based Ziegler/Natta catalyst was investigated. The univariate experiments with the central condition of 3.01 M [BD] and 0.3/0.7 of Co/Nd molar ratio incorporated with TEAL/Nd and DEAC/Nd molar ratios at 5.0 and 1.5, respectively were carried out in 1-Liter Parr reactor at 50°C for 2 h in the presence of toluene.

4.2.1 Effect of Co/Nd molar ratio

The effect of the Co/Nd molar ratio on the %conversion, Mw, MWD and microstructure of the Co/Nd-BR gum is shown in Figure 4.5 and Table 4.2. In the absence of Co (Co/Nd molar ratio = 0/1), Figure 4.5 shows that when using only the Nd catalyst for BD polymerization, only 68% conversion was achieved. While, using only Co catalyst (Co/Nd molar ratio = 1/0) could not activate the BD polymerization due to lack of enough water which is required to convert DEAC as a reactive aluminoxane acting as an electron donor for a typical BD polymerization [23, 47, 49].

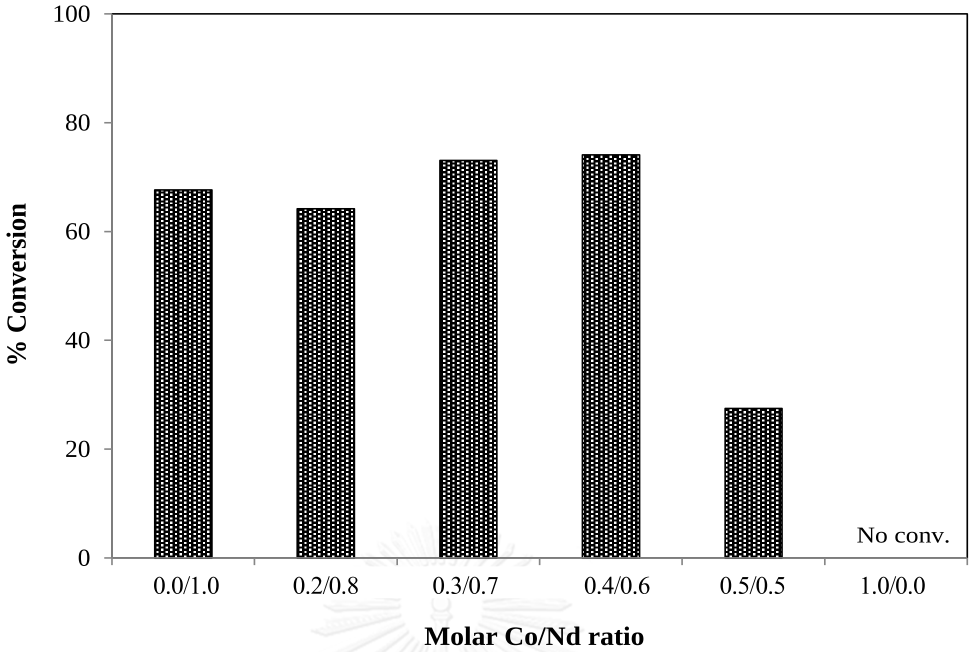


Figure 4.5 Effect of Co/Nd molar ratio on %conversion of BD polymerization: [BD] =3.01 M DEAC/Nd molar ratio =1.5, TEAL/Nd molar ratio = 5.0 at 50 °C for 2 h in toluene.

Table 4.2 Effect of the molar Co/Nd, TEAL/Nd and DEAC/Nd ratios on microstructure, Mw and MWD of the obtained BR.

Co/Nd	TEAL/Nd	DEAC/Nd	Microstructure (%)			Mw	MWD
			Cis-1,4	*Trans*-1,4	*Vinyl*-1,2	($\times 10^{-5}$)	
0.0/1.0	5.0	1.5	96.3	2.83	0.87	8.25	2.5
0.3/0.7	5.0	1.5	96.9	2.27	0.83	7.94	2.3
0.5/0.5	5.0	1.5	97.7	1.57	0.73	7.33	3.4
0.3/0.7	7.0	1.5	96.0	3.16	0.84	5.35	2.7
0.3/0.7	9.5	1.5	94.8	4.38	0.82	4.71	3.0
0.3/0.7	5.0	1.0	96.1	2.97	0.93	6.44	2.5
0.3/0.7	5.0	1.7	97.3	2.04	0.66	7.59	3.1
0.3/0.7	5.0	2.0	96.4	2.11	1.49	9.28	4.3

Condition: [BD] = 3.01 M at 50 °C for 2 h in toluene

For the Co/Nd mixed catalyst, Figure 4.5 shows that an increase in the amount of Co in the mixed Co/Nd catalyst to 0.3/0.7 or 0.4/0.6 enhanced the conversion level from 68 to 73 - 74%. This exhibited a synergetic effect between Co and Nd in the mixed catalyst. The reason for this phenomenon is still unclear. However, these results were similar to those obtained for the Ni/Nd mixed catalyst system for BD polymerization reported by Jang et al. [35]. They revealed that a molar ratio of NdV_3/nickel octoate/triisobutylaluminum/boron trifluoride-diethylether at 0.7/0.3/30/1 was preferable to produce a very high BR yield (99%) with high content of *cis*-1,4 configuration (98.5%) when the polymerization was carried out in the presence of cyclohexane at 40^{o}C for 2 h. At the critical Co content in the Co/Nd catalyst system, it was found that the Co/Nd molar ratio at 0.5/0.5 decreased the %conversion to 27.5%. Thus, it could be concluded that the appropriate Co/Nd molar ratio was 0.3/0.7 or 0.4/0.6 with 5.0 and 1.5 for the TEAL/Nd and DEAC/Nd molar ratios, respectively and > 70% conversion was achieved.

For the effect of the Co/Nd molar ratio on the microstructure, Mw and MWD of the (Co/Nd)-BR as shown in Table 4.2,indicates that an increase in the Co content in the mixed catalyst solution provided a BR with a higher content of *cis*-1,4 configuration and lower amount of both *trans*-1,4 and *vinyl*-1,2 units. This implied that the Co/Nd mixed catalyst system showed some unique properties for producing a BR structure with high *cis*-1,4 and low *vinyl*-1,2 contents with the Nd species[1] and low *trans*-1,4 structure induced by the Co portion [4, 50]. For Mw and MWD of the Co-Nd-BR, an increase in the amount of Co in the mixed catalyst solution decreased the Mw of BR from 8.25×10^5 to 7.33×10^5 when the Co/Nd molar ratio increased from 0/1 to 0.5/0.5 due to the effect of the Co catalyst producing BR with high branching and low Mw [8]. However, the increase in the Co content to 0.5/0.5 of Co/Nd molar ratio increased the MWD to 3.4. This means that this critical Co/Nd molar ratio of 0.5/0.5 could not provide a narrow MWD implying a loss of stereoregularity.

4.2.2 Effect of TEAL concentration

The effect of the TEAL concentration by varying the TEAL/Nd molar ratio from 3.0 to 9.5 on the %conversion, microstructure, Mw and MWD of the obtained Co/Nd-BR gum was evaluated and is shown in Figure 4.6 and Table 4.2.

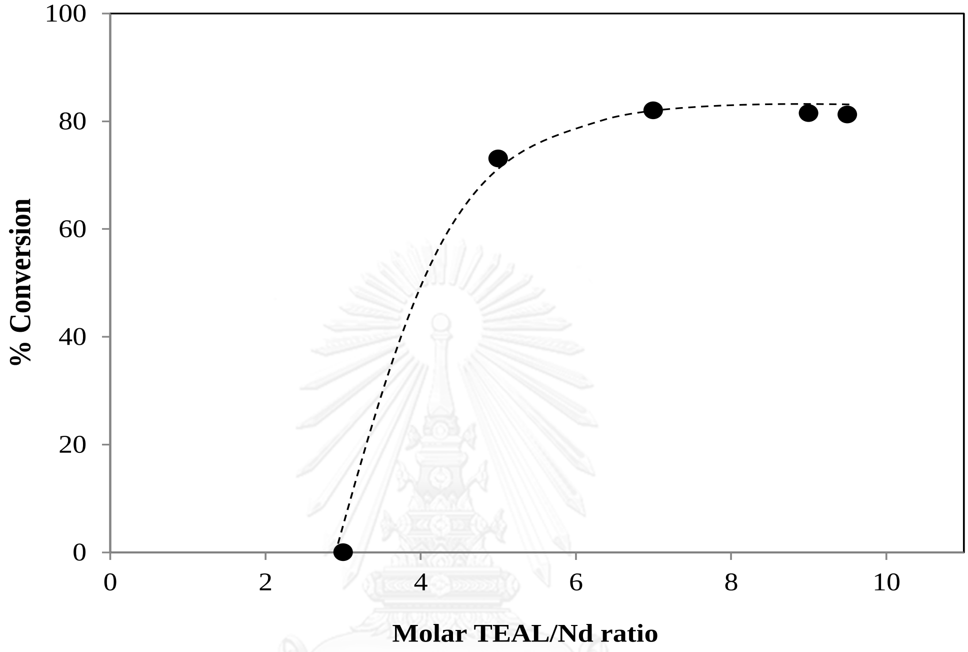


Figure 4.6 Effect of TEAL/Nd molar ratio on % conversion of BD polymerization: [BD] = 3.01 M, Co/Nd molar ratio = 0.3/0.7, DEAC/Nd molar ratio = 1.5 at 50 ºC for 2 h in toluene.

From Figure 4.6, it is seen that using a TEAL/Nd molar ratio of 3.0 was not sufficient to promote the BD polymerization. The increase in the amount of TEAL/Nd molar ratio from 5.0 to 9.5 increased the conversion from 73 to ca. 82%. It is possible that the TEAL could act as a scavenger for moisture and impurities possibly presentin the process [31, 41]. However, it was obvious that a high TEAL loading decreased the amount of *cis*-1,4 and *vinyl*-1,2 configurations, while the content of *trans*-1,4 structure of the resulting BR tended to increase. This could be explained in that an overdose of TEAL acting as an electron donor (donating alkyl group) competes with the monomer to coordinate with the metal catalyst. This induces a new BD monomer molecule which coordinates with the catalyst by using one double bond or “monodentate coordination” to form a *trans*-η^2 configuration [13, 31].

Moreover, Table 4.2 also shows that an increase in the TEAL content also decreased the MW of the Co/Nd-BR since the TEAL might be a chain transfer agent in the polymerization [13, 31]. For the MWD of the Co/Nd-BR, previous literature [51] revealed that a alkyl aluminum containing hydride moiety such as di-isobutylaluminum hydride (DIBAH) had more efficiency to control the molar mass of BR than an alkyl aluminum such as triisobutylaluminum (TIBA). This implied that the use of TEAL in the Co/Nd-based catalytic system might not effectively control the MWD of BR. The results in Table 4.2 show that the MWD of the Co/Nd-BR slightly increased from 2.3 to 3.0 when the TEAL/Nd molar ratio was increased from 5.0 to 9.5.

4.2.3 Effect of DEAC concentration

The influence of the DEAC/Nd molar ratio on %conversion, microstructure, Mw and MWD of Co/Nd-BR was investigated by varying the DEAC/Nd molar ratio over the range of 1.0 – 2.0. From Figure 4.7, it is seen that a DEAC/Nd molar ratio of 0.5 was not sufficient to activate the BD polymerization. An increase in the DEAC/Nd ratio from 1.0 to 1.7 enhanced the %conversion from 39.9 to 76.7%. This could be explained in that the DEAC was a chlorinating agent transferring chloride onto Nd and Co used as the active sites for allowing the insertion of BD as the cis-1,4 configuration [23, 52]. Thus, the amount of *cis*-1,4 units of the Co/Nd-BR slightly increased from 96.1% to 97.3% with a decreasing content of *trans*-1,4 and *vinyl*-1,2 configurations from 2.97 to 2.04% and from 0.93 to 0.66%, respectively.

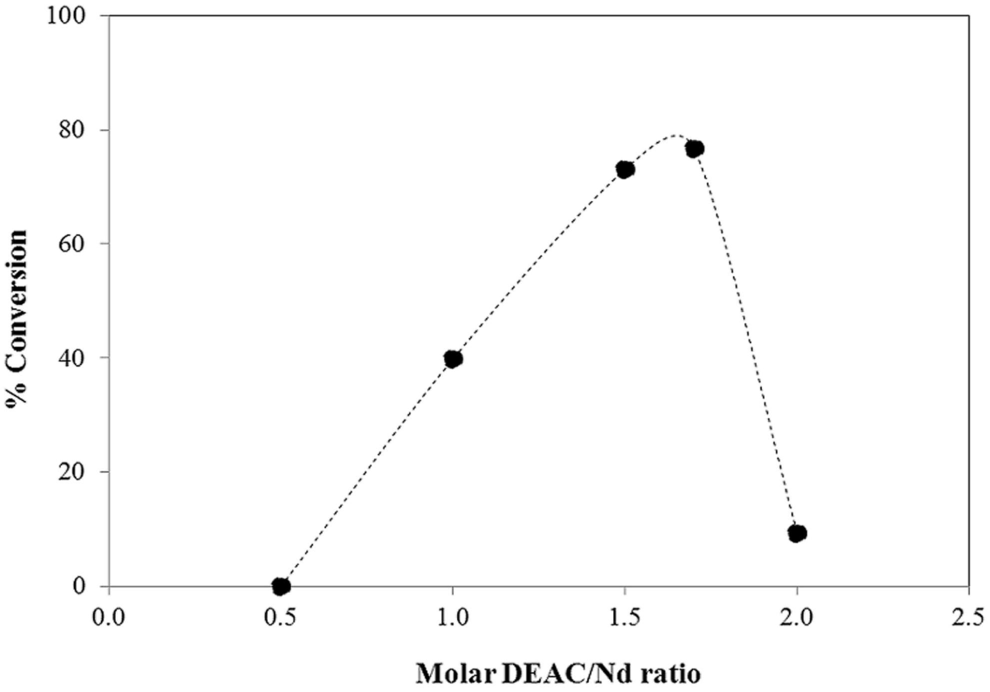


Figure 4.7 Effect of DEAC/Nd molar ratio on % conversion of BD polymerization:[BD] = 3.01 M, Co/Nd molar ratio=0.3/0.7, TEAL/Nd molar ratio=5.0 at 50 ºC for 2 h in toluene.

However, an overdose of DEAC concentration (DEAC/Nd = 2.0) drastically decreased the level of conversion to 9.3% with lower content of *cis*-1,4 units of 96.4% since the excess chlorinating agent might induce precipitation of the catalyst to form insoluble particles of $NdCl_3$ which diminish the catalytic activity [30, 52]. It was also observed that the Mw and MWD of (Co/Nd)-BR increased from 6.44×10^5 to 9.28×10^5 and 2.5 to 4.3, respectively with an increasing DEAC/Nd molar ratio from 1.0 to 2.0 due to the overchlorination of the catalyst possibly inducing catalyst precipitation which was also found in the polymerization of BD in the presence of NdV_3/*tert*-butyl chloride (*t*-BuCl)/DIBAH [53].

4.2.4 Effect of monomer concentration

The effect of BD concentration on the %conversion and physical properties of Co/Nd-BR is presented in Table 4.3. When the amount of BD increased from 2.53 to 3.31 M, the %conversion increased from 73.6% to 80.6% with increasing Mw of the obtained BR from 7.08×10^5 to 9.84×10^5. In addition, an increase in the BD concentration to 3.31 M increased the amount of *cis*-1,4 configuration to 97.5% while decreasing the content of the *trans*-1,4 structure to 1.75%. This implies that a low BD concentration could provide the appropriate reaction viscosity to promote the higher mobility of the monomer molecules favoring monodentate coordination with the metal and produced a syn complex (*trans*-1,4 form) with decreasing *cis*-1,4 configuration [5, 54]. However, the variation of the BD concentration did not affect the *vinyl*-1,2 content in the Co/Nd-BR (ca. 0.7 – 0.8%) [54].

Table 4.3 Effect of BD concentration on %conversion, microstructure, Mw and MWD of (Co/Nd)-BR gum.

[BD] (M)	%Conversion	Microstructure (%)			Mw ($\times 10^5$)	MWD
		Cis-1,4	*Trans*-1,4	*Vinyl*-1,2		
2.53	73.6	96.6	2.75	0.65	7.08	2.5
3.01	73.1	96.9	2.27	0.83	7.94	2.3
3.31	80.6	97.5	1.75	0.75	9.84	2.7

Condition: Co/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0 and DEAC/Nd molar ratio = 1.5 at 50 °C for 2 h in toluene.

4.2.5 Effect of polymerization temperature

The reaction temperature strongly affected the polymerization process in terms of %conversion, Mw and MWD of Co/Nd-BR as shown in Table 4.4. A maximum conversion of 81.8% was obtained when the polymerization temperature increased to 55 ^{o}C. Above this point (60 ^{o}C), the %conversion significantly decreased to 56.9% possibly due to catalyst deactivation. This indicated that the Co/Nd mixed catalyst in cooperation with DEAC and TEAL was easily thermally deteriorated than the NdV_3/*tert*-butyl chloride (*t*-BuCl)/DIBAH system, which deactivated above 80 ^{o}C [54]. However, the high BD conversion (81.8%) promoted by the Co/Nd mixed catalyst was achieved at a lower temperature (55 ^{o}C) than that promoted by the NdV_3/*t*-BuCl/DIBAH system which required a higher polymerization temperature (>70 – 80 ^{o}C) to reach a similar %conversion and reaction time [54].

For the effect of polymerization temperature on the microstructure of Co/Nd-BR, an increase in the reaction temperature from 45 to 60 ^{o}C slightly decreased the amount of *cis*-1,4-configuration from 97.7% at 45 ^{o}C to 96.5% with increasing formation of *trans*-1,4 and *vinyl*-1,2 configurations. This could be explained in that the higher reaction temperature promoted *cis-trans* isomerization to enhance both the *trans*-1,4 and *vinyl*-1,2 units at the expense of the *cis*-1,4 isomer [54, 55]. An increase in the reaction temperature also decreased the Mw of the Co/Nd-BR since the higher reaction temperature induced chain transfer, which led to a lower Mw with a broader MWD of the resulting BR [4, 54].

Table 4.4 Effect of polymerization temperature on %conversion, microstructure, Mw and MWD of (Co/Nd)-BR gum.

Temperature (^{o}C)	%Conversion	Microstructure (%)			Mw ($\times 10^5$)	MWD
		Cis-1,4	*Trans*-1,4	*Vinyl*-1,2		
45	66.9	97.7	2.11	0.19	8.56	2.5
50	73.1	96.9	2.27	0.83	7.94	2.3
55	81.8	97.0	2.43	0.57	7.53	2.6
60	56.9	96.5	2.69	0.81	6.86	3.0

Condition: [BD] = 3.01 M, Co/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0 and DEAC/Nd molar ratio = 1.5 for 2 h in toluene.

4.2.6 Effect of toluene/cyclohexane ratio

The selection of solvent as the media for the BD polymerization is also an important factor. The effect of the toluene/cyclohexane (w/w) ratio is presented in Table 4.5. The BD polymerization was performed under the condition as described below the Table 4.5. The results indicated that an increase in the portion of cyclohexane increased the %conversion up to 90% when the cyclohexane ratio was applied as the media of reaction. This indicated that the benzyl-H atom of toluene could be transferred to the allyl-end of the poly(butadiene) chain resulting in termination of polymeric chain propagation [56]. Figure 4.8 shows the competition between toluene or arenes and monomer to coordinate with the vacant Nd-sites [4].

Table 4.5 Effect of toluene/cyclohexane ratio (w/w) on %conversion, microstructure, Mw and MWD of (Co/Nd)-BR gum.

Toluene/cyclohexane (w/w)	%Conversion	Microstructure (%)			Mw ($\times 10^5$)	MWD
		Cis-1,4	*Trans*-1,4	*Vinyl*-1,2		
1/0	73.1	96.9	2.27	0.87	7.94	2.3
7/3	81.4	97.4	1.84	0.76	9.05	3.1
5/5	81.6	96.1	2.93	0.97	7.97	2.7
3/7	91.6	96.2	3.21	0.59	8.39	2.5
0/1	90.0	96.6	2.63	0.77	11.5	3.3

Condition: [BD] = 3.01 M, Co/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0, DEAC/Nd molar ratio = 1.5 at 50°C for 2 h

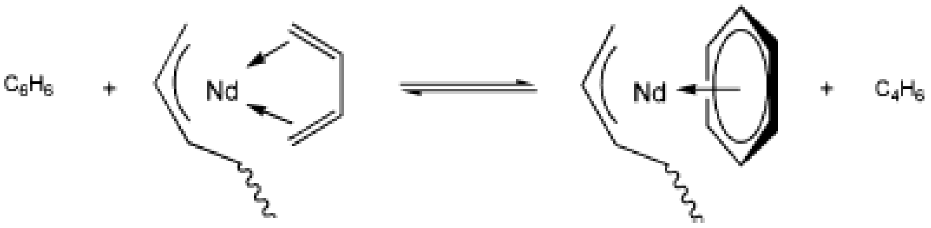


Figure 4.8 Competitive coordination to Nd between dienes and arenes [4].

However, the use of toluene, cyclohexane or a toluene/cyclohexane mixture had no significant effect on a change in the microstructure of the BR product (*cis*-1,4 = 96-97%, *trans*-1,4 = 2.3 – 2.9% and *vinyl*-1,2 = 0.8 – 0.9%). This could be explained in that the solubility parameter (∂) of BD (17.6) was quite similar for both toluene (18.3) and cyclohexane (16.8) [57]. The use of only cyclohexane as the solvent also promoted a higher Mw and MWD of the (Co/Nd)-BR to 11.5×10^5 and 3.30, respectively. This observation for the Mw of the resulting BR was different from that reported previously when using NdV_3/*t*-BuCl/DIBAH as the catalyst for the BD polymerization providing a low Mw of 2.23×10^5 due to the effect of chain transfer promoted by cyclohexane [57]. Thus, the existence of Co in the Co/Nd mixed catalyst possibly retarded the chain transferring effect when the BD polymerization was performed in cyclohexane.

4.3 Cure characteristic and Mechanical Properties of BR

Table 4.6 shows a comparison of cure characteristics and mechanical properties of Co/Nd-BR with commercial BRs: Nd-BR and Co-BR. The results showed that the Mooney viscosity of Co/Nd-BR gum (42.4) was similar to that of Nd-BR (42.9) and Co-BR (41.1).On comparing the ML and MH, it was found that there was no significant difference between Co/Nd-BR and commercial BRs. However, the MH values of Nd-BR and Co/Nd-BR were slightly higher than that of Co-BR reflecting higher hardness of the Nd-BR and Co/Nd-BR vulcanizates. This was possibly a result in that the Nd-catalyst promoted BR with lower vinyl content and more linearity in its chemical structure [2, 4]. This also resulted in a higher Mooney viscosity of the compounded BR. Moreover, the scorch time (ts_1) and optimum cure time (tc_{90}) of all BRs were similar in the range of 2.5 – 3.5 min for ts_1 and 9.6 – 10.6 min for tc_{90}.

For the mechanical properties, the Co/Nd-BR had the highest tensile strength (19.2 MPa) and ultimate elongation (470%). The improvement might be due to the influence of the Nd species in the mixed Co/Nd catalyst to providehigh *cis*-1,4 ontent with low *vinyl*-1,2 configuration and a high linear structure than for the Co species which provided high *vinyl*-1,2 content and long chain branching [20]. Moreover, the Co/Nd-BR also exhibited a higher rebound directly relating lower heat build-up and better abrasion properties, much the same as that of commercial Nd-BR.

Table 4.6 Cure characteristics and mechanical properties of BRs.

Properties	Co-BR	Nd-BR	Co/Nd-BR
Mooney viscosity (ML1+4@100^{o}C)			
BR gum	41.1	42.9	42.4
Compounded BR	66.4	77.4	83.9
Curing Properties at 160^{o}C			
ML (dN·m)	3.36	3.29	3.11
MH (dN·m)	18.3	20.2	20.1
ts_1 (min)	3.18	2.75	3.43
tc_{90} (min)	10.6	9.63	10.4
Mechanical properties			
Tensile strength (MPa)	15.2	18.8	19.2
Elongation at break (%)	400	440	470
Hardness (Cure @145 ^{o} C) (IRHD)	62	66	66
Rebound (%)	54	57	60
Abrasion (% wt loss)	8.8	7.9	8.3

4.4 Preliminary Kinetic study of BD Polymerization Using Co/Nd Mixed Catalyst

The polymerization condition for a kinetic study was carried out at 3.01 M [BD] with various Co/Nd molar ratios (0/1 to 1/0) in the presence of molar DEAC/Nd and TEAL/Nd ratios of 1.5 and 5.0, respectively. The determination of the experimental rate equation was obtained by following the change in total pressure at a constant volume system. The conversion profiles of BD polymerization using the Co/Nd mixed catalyst is shown in Figure 4.9a. The polymerization occurs quite fast during the earlier stage. Then, the polymerization rate gradually decreases with increasing %conversion of BD. The equation used for evaluation of the overall kinetics of BD polymerization is shown in Eq. 4.1:

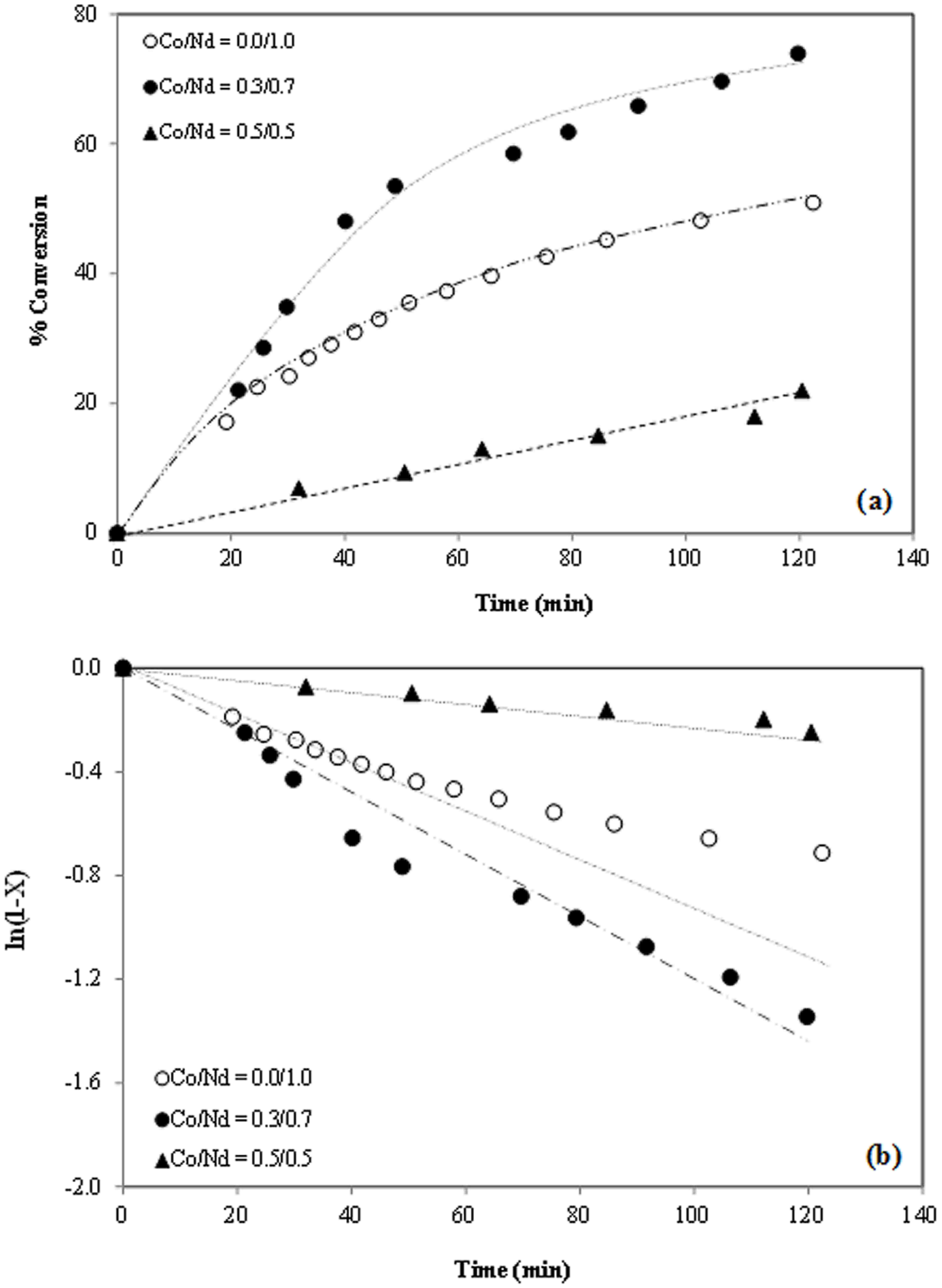


Figure 4.9 Conversion profile and ln plot of BD polymerization at various Co/Nd molar ratios:[BD] = 3.01, molar DEAC/Nd = 1.5 and TEAL/Nd molar ratio = 5.0 at 50 ºC.

$$-\frac{d[BD]}{dt} = k[1,3\text{-}BD] \tag{4.1}$$

where k is the first-order reaction rate constant for the BD polymerization. The extent of polymerization (X) was defined according to Eq. 4.2:

$$X = 1 - \frac{[1,3\text{-}BD]_t}{[1,3\text{-}BD]_0} \tag{4.2}$$

where $[BD]_t$ is the BD concentration at a given reaction time t and $[BD]_0$ is the initial BD concentration charged into the reactor. Eq. 4.1 and 4.2 can be rearranged to provide Eq. 4.3:

$$-\ln(1-X) = kt \tag{4.3}$$

Figure 4.9b shows a plot of ln(1-x) versus polymerization time for various Co/Nd molar ratios. These kinetic results indicate that the BD polymerization is first order with respect to the BD concentration when the system uses the Co/Nd mixed catalyst. The reaction rate constant was 0.90×10^{-2}, 1.55×10^{-2} and 0.20×10^{-2} min^{-1} for Co/Nd molar ratios of 0.0/1.0, 0.3/0.7 and 0.5/0.5, respectively. In the absence of Co (Co/Nd = 0/1), the ln plot versus time exhibited deviation from a straight line curve possibly due to an inappropriate TEAL content used as the co-catalyst for Nd. Rao et al. also reported that the use of TEAL as the co-catalyst of neodymium chloride tripentanolate for BD polymerization could produce high *cis*-1,4 BR (> 99%), however, only 40 – 50% conversion was obtained [44]. To evaluate the apparent activation energy of the BD polymerization using Co/Nd as the catalyst, the polymerization was carried out at 45 – 55 ºC with 3.01 M [BD] and molar ratios of Co/Nd, DEAC/Nd and TEAL/Nd at 0.3/0.7, 1.5 and 5.0, respectively. The reaction rate constant at 45, 50 and 55 ^{o}C was calculated as 1.37×10^{-2}, 1.55×10^{-2} and 1.84×10^{-2} s^{-1}, respectively. However, an increase in the polymerization temperature above 55ºC decreased the polymerization rate possibly due to the deactivation of the catalytic active sites. This behavior was similar to that reported in previous literature for a Co-based catalyst which was preferred to operate at a polymerization temperature of 15 – 55 ^{o}C [58]. The ln plot shown in Figure 4.10 indicated that the apparent activation energy (Ea) of the BD polymerization catalyzed with the Co/Nd-based Ziegler-Natta catalyst calculated from the Arrhenius's equation was 25.6 kJ/mol following detail in Appendix D (Table D-1 and Figure D-1). The low value of Ea reflected that this polymerization system was under a mass-transfer limitation [59].The low Ea value was also found for a typical BD polymerization using a Co-containing catalyst (25.1 kJ/mol) [60] or Ni-based system (58.9 kJ/mol) [27].

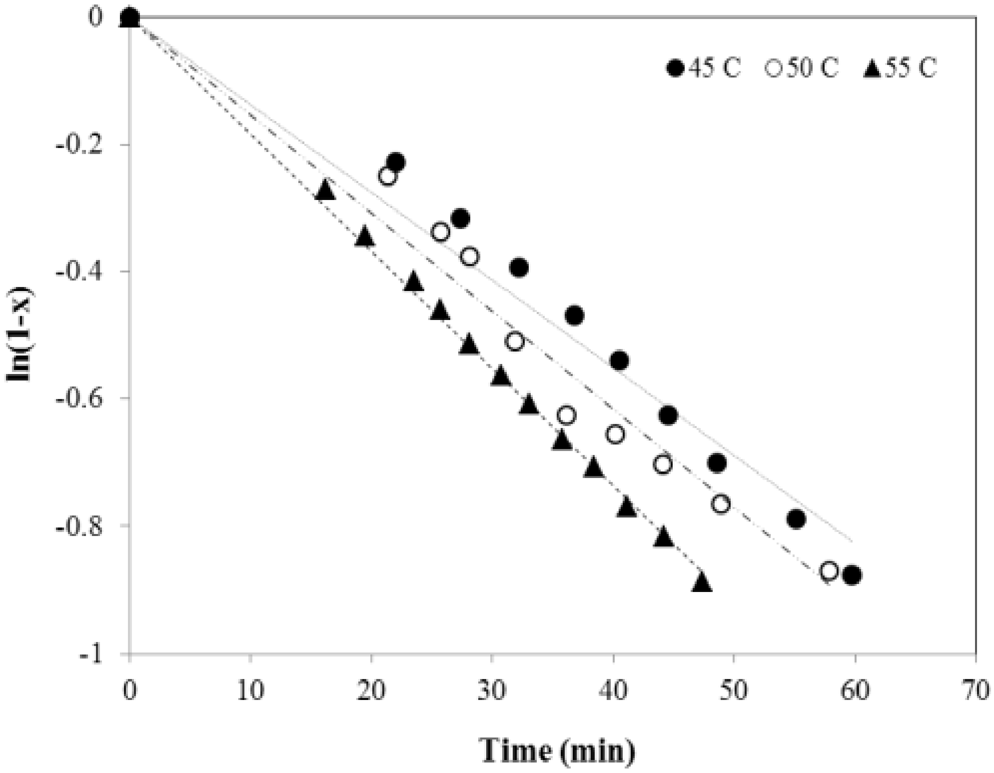


Figure 4.10 Conversion profile and ln plot of BD polymerization at various Co/Nd molar ratios: [BD] = 3.01, DEAC/Nd molar ratio = 1.5 and TEAL/Nd molar ratio = 5.0 at 50 ºC.

CHAPTER V

PERFORMANCE OF Ni/Nd-BASED ZIEGLER-NATTA CATALYST ON MICROSTRUCTURE CONFIGURATIONS AND PROPERTIES OF BUTADIENE RUBBER

Conventional 1,3-butadiene (BD) polymerization using nickel (Ni)-based catalyst system produces butadiene rubber (Ni-BR) containing a high content of *cis*-1,4 configuration (ca. 96 – 98%) with high branching, broad molecular weight distribution and low cold flow to promote easier processing than a BR having a more linear structure [2-4, 11]. The chemical structure of Ni-BR also consists of a fairly high level of *trans*-1,4 units (ca. 3%) and low level of *vinyl*-1,2 units (ca. 1%) [4, 14]. This polymerization system is comprised of nickel naphthenate, boron fluoride etherate ($BF_3{\cdot}Et_2O$) and trialkylalumimium, which is carried out in solution such as aliphatic and aromatic solvents [27]. However, this process releases more butadiene dimer (4-vinyl cyclohexene) (Figure 5.1) [61], which is harmful to the environment, than the polymerization process using lanthanide catalysts [5]. Moreover, the fluorine-containing co-catalyst, such as hydrogen fluoride (HF) or $BF_3{\cdot}Et_2O$ required for the Ni-based catalyst system generates strong acid when it contacts water. This can induce equipment corrosion and possible gel-formation in the obtained polymer [62]. The high gel content of Ni-BR (> 0.05%) also limits its application for the production of high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) resin [4]. Although Ni-BR has a high degree of branching to provide ease of processing, its tensile strength and fatigue resistance are low [14].

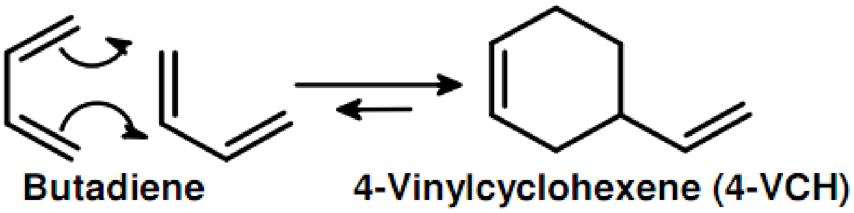


Figure 5.1 Formation of 4-vinyl cyclohexene [61].

For lanthanide-based Ziegler-Natta catalysts such as neodymium (Nd) coordinating with aluminum halides acting as co-catalysts for BD polymerization, the obtained BR (Nd-BR) has high linearity with high *cis*-1,4 microstructure (ca. 99%) and a very low amount of *vinyl*-1,2 units (< 1%). The glass transition temperature (T_g) of Nd-BR was the lowest at ca. -109 ºC, which is advantageous for applications in very low temperature environments [4]. Moreover, this catalyst type has a high solubility in saturated alkanes, which are safer and more environmental friendly than benzene and toluene normally used as in conventional BD polymerization [5]. This system also promotes high monomer conversion (ca.100%) without gel formation in the resulting product and releases less content of vinyl cyclohexene [5].

To combine the desired inherent properties of Ni-BR and Nd-BR, this research work was aimed at a study of the performance of a mixed catalyst containing both Ni and Nd (Ni/Nd) coordinating with diethyl aluminum chloride (DEAC) and triethyl aluminum (TEAL) used as co-catalysts for BD polymerization. The effects of parameters such as Ni/Nd molar ratio, amounts of co-catalyst and chlorinating agent, reaction temperature and solvent type on BD conversion and microstructure including molecular weight (Mw) and molecular weight distribution (MWD) of the obtained BR gum (Ni/Nd-BR) were investigated. The vulcanization and mechanical properties of the Ni/Nd-BR vulcanizates were also examined and compared to those of commercial BRs obtained from Ni and Nd-based polymerization processes.

5.1 Chemical Structures, T_g and Gel content of Ni/Nd-BR

Chemical structure in terms of *cis*-1,4, *trans*-1,4 and *vinyl*-1,2 units in the Ni/Nd-BR produced from BD polymerization at 50 ^{o}C using the Ni/Nd-based catalyst system at a molar ratio of 0.3/0.7 with 1.5/1.0 and 5.0/1.0 DEAC/Nd and TEAL/Nd molar ratios, respectively was examined by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (Figure 5.2), proton (^{1}H-NMR, Figure 5.3a) and carbon (^{13}C-NMR, Figure 5.3b) nuclear magnetic resonance spectroscopy. The *results* were also compared to those of commercial BRs prepared by BD polymerization using Ni and Nd-based Ziegler-Natta catalysts.

Figure 5.2 shows the ATR- FTIR spectra of all BR samples. It indicates high intensity of the absorption peak at 738.5 cm^{-1} reflecting a high level of *cis*-1,4 configuration in the range of 96 – 98% (Table 5.1). The *cis*-1,4 unit content in the Ni/Nd-BR at 96.6% conversion was in the same range as that of commercial Nd-BR (97.6%) and Ni-BR (96.3%). Regarding the absorption peak at 965 cm$^{-1,}$ attributed to the *vinyl*-1,2 structure, the intensity of this structure for Ni/Nd-BR (0.33%) was lower than that of the commercial Ni-BR (1.80%). It indicated that the Ni/Nd mixed catalyst could promote a high content of *cis*-1,4 units with a very low amount of *vinyl*-1,2 configuration. This could be explained in that the high performance of Nd in the Ni/Nd mixed catalyst induced a high polymerization rate to form an external σ-allyl species rather than an internal one resulting in a decrease in the opportunity to form *vinyl*-1,2 structure in BR [44]. However, the intensity of the absorption peak at 910 cm^{-1} attributed to the *trans*-1,4 configuration of Ni/Nd-BR was highest. It can be seen that the amount of *trans*-1,4 units in the Ni/Nd-BR was 3.26%, which was higher than that of commercial BRs (1.90% for Ni-BR and 2.12% for Nd-BR). Similar results were earlier reported for BR produced by a Ni-based Ziegler-Natta catalyst, usually having a high amount of *trans*-1,4 configuration which is influenced by Ni [8, 14].

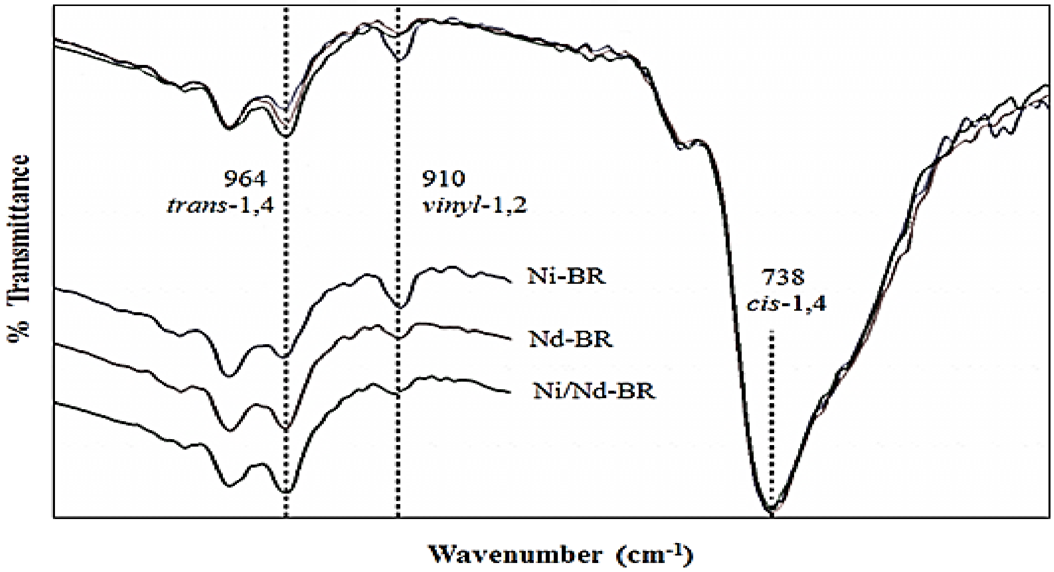


Figure 5.2 Comparative ATR-FTIR spectra of Ni/Nd-BR and commercial BRs: Ni-BR and Nd-BR.

Table 5.1 Microstructure, T_g and gel content of BRs.

BR	Microstructure (%)			T_g	Gel content
	Cis-1,4	*Trans*-1,4	*Vinyl*-1,2	(◦C)	(%)
Ni-BR[a]	96.3	1.90	1.80	-110.4	1.47
Nd-BR[b]	97.6	2.12	0.28	-111.0	0
(Ni/Nd)-BR[c]	96.6	3.26	0.14	-110.8	0.55

[a] Commercial BR obtained from BST Elastomer Co., Ltd

[b] Commercial BR obtained from Lanxess Co., Ltd

[c] BR prepared from Ni/Nd-based catalyst (Condition: [BD] = 3.01 M, Ni/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0/1.0 and DEAC/Nd molar ratio = 1.5/1.0 at 50 °C for 2 h in toluene).

The microstructure of Ni/Nd-BR was also determined by using ^{1}H-NMR and ^{13}C-NMR spectroscopy and compared to those of commercial BRs as shown in Figure 5.3a and 5.3b, respectively. The ^{1}H-NMR spectra of all BR samples (Figure 5.3a) showed signals in the range of 4.8 – 5.2 ppm and 5.2 – 5.8 ppm, which are assigned to $=CH_2$ of the *vinyl*-1,2 configuration and –CH= of 1,4-butadiene and 1,2-butadiene units [45,46], respectively. The results also showed that the signal for $=CH_2$ of the *vinyl*-1,2 configuration of Nd-BR and Ni/Nd-BR was lower than those of Ni-BR. From the ^{13}C-NMR spectra of all BR samples (Figure 5.3b), the microstructure of these samples showed peaks at 27.4, 32.7 and 34.0 ppm attributed to the *cis*-1,4, *trans*-1,4 and *vinyl*-1,2 configurations, respectively [47]. This was consistent to the results observed from ATR-FTIR and ^{1}H-NMR spectroscopy showing a very low intensity of the *vinyl*-1,2 structure signal for the Nd-BR and Ni/Nd-BR samples.

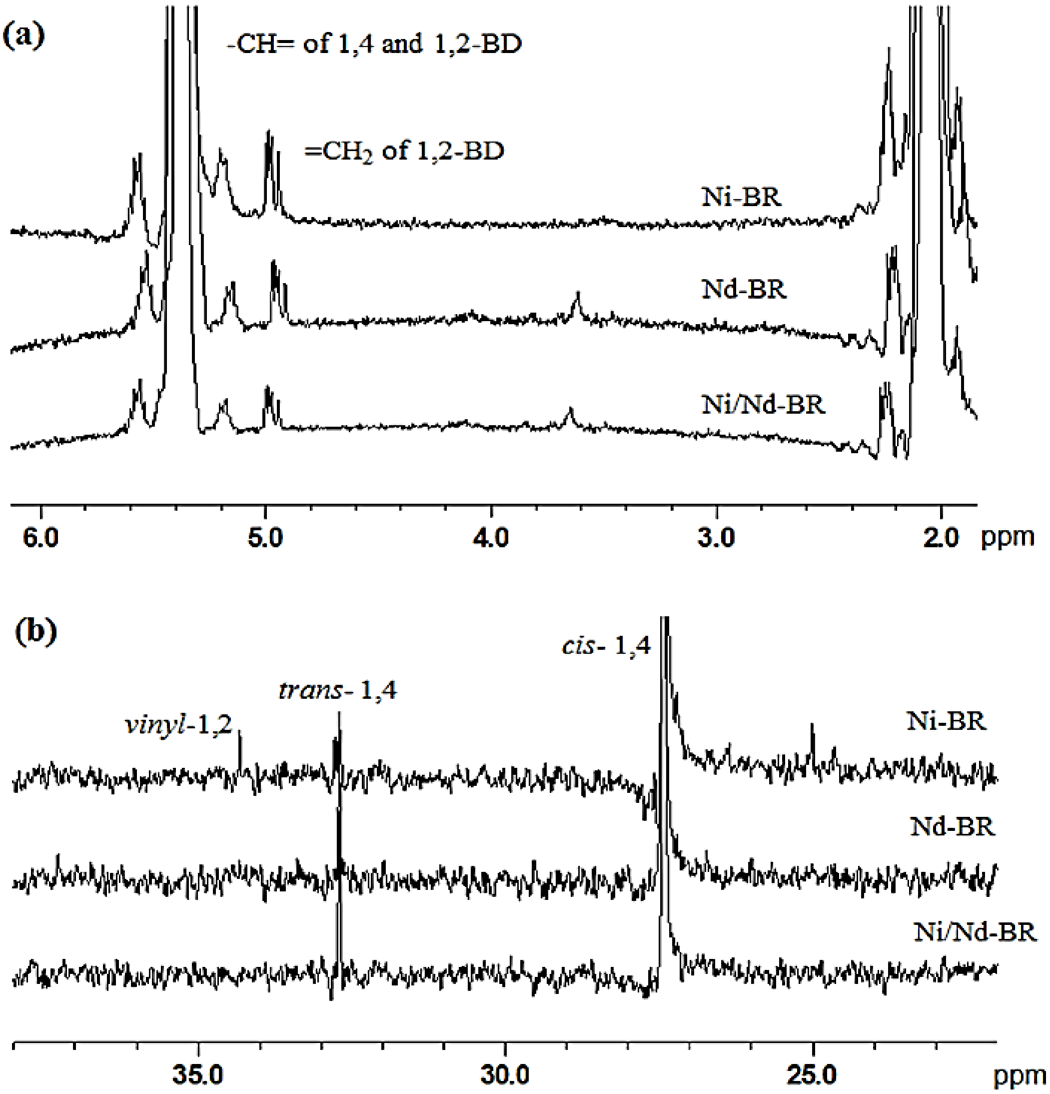


Figure 5.3 Chemical structure of BRs comparatively analyzed by (a) ^{1}H-NMR and (b) ^{13}C-NMR spectroscopy.

For the evaluation of the glass transition temperature (T_g), Table 5.1 shows that the T_g values for all BR samples were in the range of -110 to -111^{o}C. Generally, the T_g of these materials is dependent on the structural arrangement. It has been reported that BR containing high contents of *cis*-1,4 and *trans*-1,4 configurations have a low T_g value (ca. -106 to -107 ^{o}C), whereas BR with a high amount of the *vinyl*-1,2 unit in the structure of 1,2-atactic or 1,2-syndiotactic BR had higher T_g values such as -4 or -28 ^{o}C, respectively [3]. From the measurement of gel content (Table 5.1), the gel content of Ni/Nd-BR (0.55%) was much lower than that of commercial Ni-BR (1.47%). This implied that the existing *vinyl*-1,2 configuration could induce gel formation via re-incorporation of internal unsaturation units for the Ni-BR system [8, 48].

5.2 BD Polymerization Using Ni/Nd-Based Ziegler-Natta Catalyst

The effect of parameters on BD polymerization using the Ni/Nd-based Ziegler-Natta catalyst in terms of BD conversion and physical properties of the obtained Ni/Nd-BR gum were investigated. Univariate experiments of BD polymerization with the central condition of 3.01 M of BD and 0.3/0.7 of Ni/Nd molar ratio in conjunction with molar ratios of TEAL/Nd and DEAC/Nd of 5.0/1.0 and 1.5/1.0, respectively were performed in the presence of toluene at 50 ^{o}C for 2 h.

5.2.1 Effect of catalyst components

The effect of catalyst components such as the molar ratios of Ni/Nd, TEAL/Nd and DEAC/Nd on the BD polymerization in terms of conversion, microstructure, Mw and MWD of the obtained Ni/Nd-BR gum are shown in Figure 5.4 and Table 5.2.

For the effect of the Ni/Nd molar ratio on BD conversion (Figure 5.4a), it was found that the use of only Nd species induced BD polymerization with 76.3% conversion. The obtained BR gum had 95.3% *cis*-1,4 and 0.26% *vinyl*-1,2 configurations with a fairly high level of *trans*-1,4 units (4.44%) (Table 5.2). Generally, the Nd catalyst coordinated with triethylaluminum chloride (Et_3AlCl_3) and diisobutylaluminum hydride (Al^iBu_2H) ($Nd(OCOR)_3/Et_3AlCl_3/ Al^iBu_2H = 1/1/8$) could provide a BR with 98% *cis*-1,4 unit and 1% *trans*-1,4 configuration [4]. In our work, it was possible that the co-catalysts (DEAC and TEAL) applied in this system were not appropriate for the Nd-based catalyst to produce BR with a high *cis*-1,4 structure and a low level of *trans*-1,4 units. When the amount of Ni species was increased in the mixed Ni/Nd-based catalyst, the BD conversion increased approaching a maximum value of 84% at a 0.2/0.8 Ni/Nd molar ratio. Above this point, the conversion tended to decrease and no polymeric product formed when only the Ni species was applied for BD polymerization (Ni/Nd molar ratio = 1.0/0.0). This is due to the fact that this system lacked the addition of water, which is normally

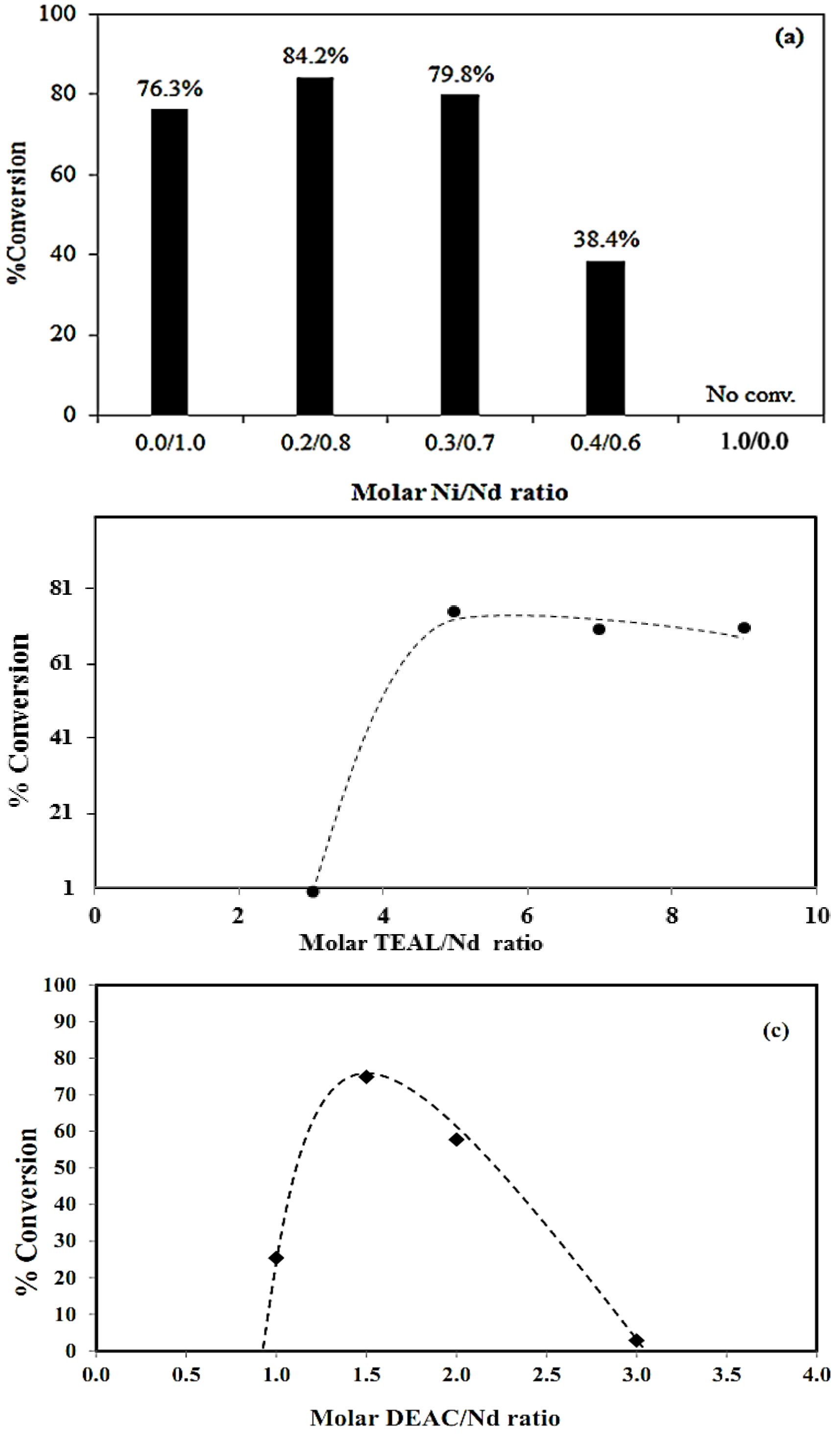


Figure 5.4 Effect of the catalyst components on conversion: (a)molar Ni/Nd ratio, (b)TEAL/Nd molar ratio and (c) DEAC/Nd molar ratio (Condition: [BD] = 3.01 M at 50 °C for 2 h in toluene).

Table 5.2 Effect of the catalyst components on microstructure, Mw and MWD of Ni/Nd- BR gum.

Ni/Nd	TEAL/Nd	DEAC/Nd	Microstructure (%)			Mw	MWD
			Cis-1,4	*Trans*-1,4	*Vinyl*-1,2	(x 10^5)	
0.0/1.0	5.0/1.0	1.5/1.0	95.3	4.44	0.26	6.89	2.5
0.2/0.8	5.0/1.0	1.5/1.0	94.8	4.93	0.27	5.89	2.2
0.3/0.7	5.0/1.0	1.5/1.0	96.6	3.26	0.14	5.22	2.4
0.4/0.6	5.0/1.0	1.5/1.0	96.8	3.07	0.13	5.82	3.6
0.3/0.7	7.0/1.0	1.5/1.0	96.0	3.80	0.20	6.06	2.6
0.3/0.7	9.0/1.0	1.5/1.0	97.2	2.52	0.28	7.10	2.8
0.3/0.7	5.0/1.0	1.0/1.0	96.6	3.42	0.03	6.15	2.8
0.3/0.7	5.0/1.0	2.0/1.0	96.4	3.45	0.15	5.10	2.4
0.3/0.7	5.0/1.0	3.0/1.0	97.0	2.32	0.68	13.1	13.4

Condition: [BD] = 3.01 M at 50 ºC for 2 h in toluene

required to convert DEAC to a reactive aluminoxane, which is an electron donor for a typical BD polymerization [47, 63]. Moreover, the use of a chlorinating agent such as DEAC might be inappropriate for Ni in BD polymerization since a fluorine-containing substance such as $BF_3{\cdot}Et_2O$ is the best Lewis acid used as the co-catalyst for the Ni-based catalyst system [27, 37].

For the microstructure and physical properties of the obtained Ni/Nd-BR (Table 5.2), when the Ni content in the mixed catalyst solution increased from a Ni/Nd molar ratio of 0.2/0.8 to 0.4/0.6, the content of *cis*-1,4 configuration in the Ni/Nd-BR increased slightly from ca. 95 to 97%, while the amount of *trans*-1,4 and *vinyl*-1,2 units decreased from ca. 5% to 3% and 0.3% to 0.1%, respectively. This is due to a synergistic effect from both Nd and Ni species to form BR with a higher content of *cis*-1,4 configuration and lower amount of *vinyl*-1,2 units [2, 4, 8]. Thus, it is apparent that this Ni/Nd mixed catalyst system exhibited specific properties to produce BR containing a high content of *cis*-1,4 configuration with a low amount of *vinyl*-1,2 units (< 0.3%). It was also found that the Ni/Nd-BR produced from the BD polymerization using the mixed catalyst solution with a higher Ni content (Ni/Nd molar ratio = 0.3/0.7 - 0.4/0.6) had a lower Mw (5.22 x 10^5 - 5.89 x 10^5) with a broader MWD (2.4 – 3.6) than the BR produced by using only the Nd-based catalyst.

This can be explained in that the Ni catalyst could produce BR with lower linearity and molecular weight than BR generally produced by the Nd-based catalyst [2, 4]. In addition, the higher MWD of the Ni/Nd-BR produced by the mixed Ni/Nd catalyst solution with higher Ni content indicated the loss of stereoregularity control of the polymeric product.

For the effect of TEAL concentration on the conversion of BD polymerization (Figure 5.4b), the use of TEAL/Nd molar ratio at 3.0/1.0 was not sufficient to activate the BD polymerization. When the TEAL/Nd molar ratio increased from 5.0/1.0 to 9.0/1.0, the conversion increased to ca. 70 – 75% since TEAL could act as the oxygen and moisture scavenger in the system [31]. It was also found that the increase in the TEAL/Nd molar ratio slightly affected the *cis*-1,4 microstructure of the obtained Ni/Nd-BR (%*cis*-1,4 = 96 – 97%). Although previous work has reported that the use of a chlorine-containing co-catalyst such as TEAL gave low efficiency for the Ni-based catalyst system to produce high *cis*-1,4 BR (%*cis*-1,4 = 85%) [31], this type of co-catalyst such as TEAL in the mixed Ni/Nd catalyst system was safer to handle than the cumbersome fluorine-containing co-catalyst [62]. However, it is still unclear whether the higher TEAL concentration induced lower contents of *trans*-1,4 and *vinyl*-1,2 units. Moreover, it was observed that the increase in TEAL/Nd molar ratio from 5.0/1.0 to 9.0/1.0 yielded an increase in Mw (from 5.22×10^5 to 7.10×10^5) and MWD (from 2.2 to 2.6) of the product. Normally, alkylaluminum compounds can act as an electron donor to occupy one coordination site via monodentate coordination, resulting in the subsequent coordination of the new incoming monomer with only one double bond to form a *trans*-1,4 unit (Figure 5.5) and it is also used as a chain transfer agent to decrease the polymer molar mass [64]. It can be assumed that some portion of the Ni in the mixed Ni/Nd catalyst was possibly sacrificed to inhibit the TEAL effect to promote the formation of the *trans*-1,4 structure as well as a chain transfer effect.

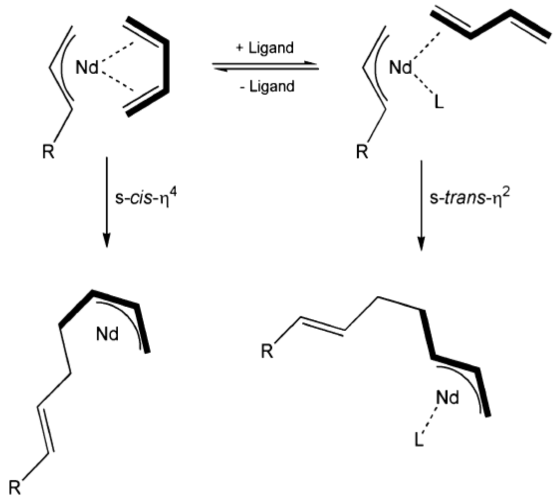


Figure 5.5 Influence of electron donors on the microstructure of BR [4].

The effect of DEAC concentration on the conversion of BD polymerization and the physical properties of the Ni/Nd-BR is shown in Figure 5.4c and Table 5.2. Figure 5.3c, suggested that BD polymerization did not occur when a DEAC/Nd molar ratio of 0.5/1.0 was used. When the DEAC/Nd molar ratio increased to 1.5/1.0, a maximum monomer conversion of 74.8% was obtained. This can be explained in that DEAC acts as the chlorinating agent to transfer chloride onto Nd to provide the active sites for the insertion of the BD monomer to a form *cis*-1,4 configuration [52]. However, an overdose of DEAC concentration at a DEAC/Nd molar ratio of 2.0/1.0 and 3.0/1.0 drastically decreased the conversion to 57.7% and 2.8%, respectively possibly due to catalyst precipitation to form insoluble $NdCl_3$ particles, which decreased the catalytic activity [20]. For the effect of the DEAC concentration on the microstructure of the Ni/Nd-BR (Table 5.2), an increase in the DEAC concentration did not significantly affect the *cis*-1,4 configuration. However, an increase in the DEAC concentration decreased the amount of *trans*-1,4 unist while the amount of the 1,2-*vinyl* configuration slightly increased. This behavior was similar to the BD polymerization catalyzed by Nd/diisobutyl aluminium hydride (DIBAH)/ethylaluminium sesquichloride (EASC) in that the existence of the halide species promoted the production of BR with a low *trans*-1,4 content [18]. Considering the Mw and MWD, when the DEAC/Nd molar ratio increased (1.5/1.0 - 2.0/1.0),while the Mw and MWD of the obtained Ni/Nd-BR decreased. Here the

DEAC acted as a chain transferring agent in the polymerization [53]. However, with an overdose of DEAC concentration at a DEAC/Nd molar ratio of 3.0/1.0, the BR produced had a very high Mw (13.1 x 10^5) with a broad MWD (13.4). This phenomenon has also been reported for the BD polymerization when using NdV_3/*tert*-butyl chloride (t-BuCl)/ DIBAH [53].

5.2.2 Effect of reaction parameters

The influence of reaction parameters such as BD concentration, reaction temperature and toluene/cyclohexane ratio on BD conversion, microstructure, Mw and MWD of the Ni/Nd-BR gum is summarized in Table 5.3.

For the effect of BD loading, an increase in the BD concentration from 2.53 M to 3.31 M enhanced the conversion from 47.4 to 80.5%. It was also observed that the content of *cis*-1,4 configuration increased from 94.9 to 96.6% and the amount of *trans*-1,4 units decreased from 4.91 to 3.26% on increasing the BD concentration from 2.53 to 3.31 M. This could be explained in that the increase in the BD concentration possibly increased the reaction medium viscosity resulting in a lower mobility of the BD molecule, which could promote monodentate coordination with the catalyst site to form a *trans*-1,4 configuration [54]. However, the content of *cis*-1,4 units decreased to 93.9% with an increasing amount of *trans*-1,4 (5.77%) and *vinyl*-1,2(0.33%) structures when the BD concentration was increased to 3.31 M. It is possible that the Ni species in the Ni/Nd mixed catalyst had more influence favoring a higher amount of *trans*-1,4 and *vinyl*-1,2 configurations than the Nd species [2, 14, 44]. For the Mw and MWD evaluation

Table 5.3 Effect of the reaction parameters on microstructure, MW and MWD of Ni/Nd- BR gum.

[BD] (M)	Temp. (°C)	Toluene/cyclohexane (w/w)	Conversion (%)	Microstructure (%)			Mw (x 10^5)	MWD
				Cis-1,4	*Trans*-1,4	*Vinyl*-1,2		
2.53	50	1.0/0.0	47.4	94.9	4.91	0.19	4.22	2.4
3.01	50	1.0/0.0	74.8	96.6	3.26	0.14	5.22	2.4
3.31	50	1.0/0.0	80.5	93.6	5.77	0.33	3.95	2.4
3.01	45	1.0/0.0	66.1	95.5	4.23	0.27	5.12	2.6
3.01	60	1.0/0.0	80.0	94.0	5.44	0.56	4.19	3.0
3.01	50	0.7/0.3	82.2	96.4	3.41	0.19	5.97	3.1
3.01	50	0.3/0.7	98.9	96.4	3.49	0.11	8.55	3.1
3.01	50	0.0/1.0	100	95.6	4.33	0.07	10.8	2.8

Condition: Ni/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0/1.0, DEAC/Nd molar ratio = 1.5/1.0, reaction time = 2 h

(Table 5.3), the Mw of Ni/Nd-BR increased from 4.22 x 10^5 to 5.22 x 10^5 on increasing the BD loading from 2.53 to 3.01 M. However, when the BD concentration was increased to 3.31 M, the Mw of the obtained Ni/Nd-BR decreased to 3.95 x 10^5 possibly due to the more difficult mobility of the catalysts in the reaction media containing a higher monomer concentration [54]. However, the MWD of the obtained Ni/Nd-BR did not change with the BD loading.

The effect of reaction temperature (40 – 60 °C) on the conversion and the physical properties of Ni/Nd-BR is presented in Table 5.3. The results indicated that the conversion increased from 66.1% to 80.0% on increasing the reaction temperature from 45 to 60 ºC. On comparing with our previous work [65], Co/Nd-based Ziegler-Natta catalyst could activate BD polymerization at 55°C to achieve the same conversion (ca. 80%) as with the Ni/Nd catalyst system. This implies that the Ni/Nd mixed catalyst in corporation with DEAC and TEAL had higher resistance to thermal decomposition than the Co/Nd mixed catalyst system. From a microstructure evaluation, the content of *cis*-1,4 units slightly decreased with increasing temperature possibly due to the enhancement of the *cis-trans* isomerization rate promoting the formation of *trans*-1,4 and *vinyl*-1,2 configurations [54]. It was also observed that when the reaction temperature increased, the Mw of Ni/Nd-BR decreased while the

MWD increased. This could be explained in that the higher temperature promoted the effect of a chain transfer reaction resulting in a decrease in the Mw of polymer with a higher degree of chain branching and an increasing MWD of the obtained polymeric product [54].

The solvent media used for the polymerization is also an important factor for the product yield and stereospecificity of the obtained product [34, 66]. Many solvents are applied in BD polymerization such as aliphatic, cycloaliphatic and aromatic hydrocarbons. The aromatic hydrocarbons have lower reactivity than aliphatic and cycloaliphatic solvents due to a higher efficiency to competitively coordinate with catalytic active sites than the monomers. Aromatic solvents, such as toluene ,have higher boiling points (ca. 110 – 111 ^{o}C), which are safer than the aliphatic ones having lower boiling point such as hexane (ca. 69 ^{o}C). Thus, our work was aimed at increasing the efficiency of toluene by mixing it with a chain closed aliphatic solvent such cyclohexane (boiling point = ca. 80 – 81^{o}C). From Table 3, the conversion increased from 74.8% to 100% when the cyclohexane amount in the reaction media was increased from 1.0/0.0 to 0.0/1.0 (w/w) toluene/cyclohexane. This implied that cyclohexane was more appropriate for BD polymerization than toluene since the benzyl-H atom of toluene could be transferred to the allyl-end of the BD chain resulting in the termination of the polymer chain propagation [56].

For the effect of solvents on the microstructure, the use of toluene, cyclohexane and their mixture at various ratios had no significant effect on *cis*-1,4 unit (95 – 96%). However, when the cyclohexane amount increased from 1.0/0.0 to 0.0/1.0 (w/w) in the toluene/cyclohexane mixture, the amount of *trans*-1,4 unit slightly increased from 3.41% to 4.33% with significant decrease in the amount of *vinyl*-1,2 structure from 0.19% to 0.07%. This implied that the use of cyclohexane as the media for BD polymerization could promote the influence of Ni in the Ni/Nd-based catalyst to produce BR with a higher amount of *trans*-1,4 configuration. Moreover, cyclohexane facilitated both Ni and Nd species performance to suppress the formation of *vinyl*-1,2 units in the obtained Ni/Nd-BR product. From the GPC chromatograms as shown in Figure 5.6, the Mw of the Ni/Nd-BR increased from 5.97 x 10^5 to 10.8 x 10^5 with a slight change in MWD when the cyclohexane amount was increased. Previous work has reported that cyclohexane in the NdV_3/*t*-BuCl/DIBAH system could promote chain transfer resulting in a reduction in the Mw of BR with a higher MWD value [34]. On comparing with this work, it can be postulated that that the use of the Ni/Nd-based catalyst possibly suppresses the chain transfer effect of the cyclohexane and also reduces the formation of chain branching resulting in the MWD reduction observed for the Ni/Nd-BR.

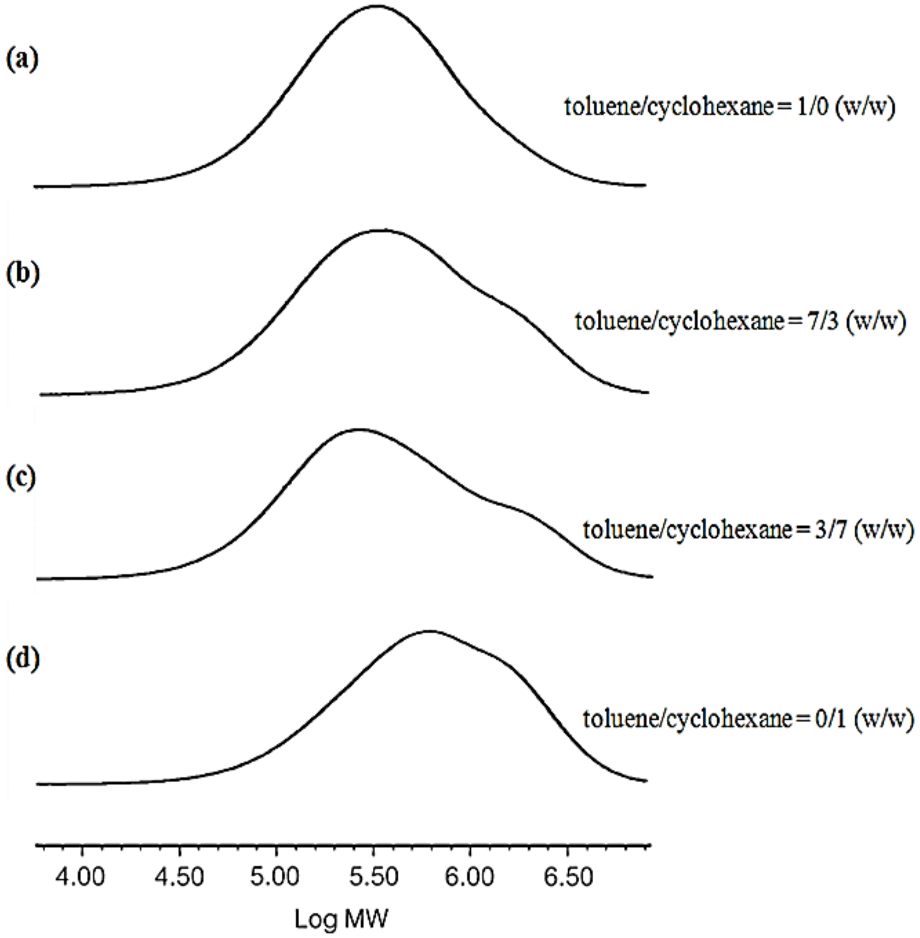


Figure 5.6 GPC chromatograms of the Ni/Nd-BR produced in the presence of toluene/cyclohexane at various wt ratios.

5.3 Vulcanization of Ni/Nd-BR: Cure Characteristics and Mechanical Properties

The cure characteristics and mechanical properties of Ni/Nd-BR compared with commercial Ni-BR and Nd-BR are presented in Table5.4. The Nd-BR and Ni/Nd-BR had higher M_L and M_H values than Ni-BR due to the influence of the Nd catalyst which provided a BR with higher linearity and *cis*-1,4 unit content [2]. However, the Ni/Nd-BR had a scorch time (ts_1) and optimum cure time (tc_{90}) similar to the commercial BRs (ca. 2.3 min and 6.4 min for ts_1 and tc_{90}, respectively). From the mechanical performance of these BR samples, Ni/Nd-BR had the highest tensile strength (15.4 MPa), elongation at break (444%) and hardness (62.5) with the lowest volume loss during testing of abrasion resistance (21.3 mm^3). These excellent properties were attributed to the high *cis-1,4* and *trans*-1,4 configurations of the Ni/Nd-BR resulting from the influence of both Nd and Ni species. The relatively high amount of *trans*-1,4 units also promoted a higher crystallinity in the polymer backbone to induce increased hardness and abrasion resistance of BR [8, 67, 68].

Table 5.4 Cure characteristics and mechanical properties of BR vulcanizates.

Properties	Ni-BR[a]	Nd-BR[b]	Ni/Nd-BR[c]
Curing characteristics at 160 °C			
M_L (dN m)	2.84	2.97	2.95
M_H (dN m)	16.8	17.5	16.9
ts_1 (min)	2.37	2.32	2.37
tc_{90} (min)	6.40	6.44	6.39
Mechanical properties			
Tensile strength (MPa)	13.9	13.8	15.4
Elongation at break (%)	434	379	444
Hardness (Shore A)	59.3	61.0	62.5
Abrasion resistance (volume loss, mm^3)	25.3	20.9	21.3

[a] Commercial BR obtained from BST Elastomer Co., Ltd

[b] Commercial BR obtained from Lanxess Co., Ltd

[c] BR prepared from Ni/Nd-based catalyst (Condition: [BD] = 3.01 M, Ni/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0/1.0 and DEAC/Nd molar ratio = 1.5/1.0 at 50 °C for 2 h in toluene).

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

6.1.1 Preliminary study for 1,3-butadiene polymerization using Nd- and Co/Nd-catalyst system

A green color was found when NdV_3 coordinated with DEAC and TEAL. This is possibly due to that DEAC and TEAL acting as a Lewis acid changed the ionic characteristics of Nd^{3+} to Nd^{2+}. The (Co/Nd) mixed catalyst coordinated with DEAC and TEAL, the color changed to a yellow black color due to DEAC and TEAL acting as a Lewis acid. A BD conversion of higher than 90% was obtained on increasing the molar ratio of Co/Nd from 0.1 to 0.4 when the molar ratios of DEAC/Nd and TEAL/Nd were kept constant at 1.6 and 5.1, respectively. A BR with a high *cis*-1,4 content at 94-95 % was obtained from this mixed catalyst system.

6.1.2 1,3-Butadiene polymerization using Co/Nd-based Ziegler-Natta catalyst

The Co/Nd-based Ziegler-Natta catalyst coordinated with diethylaluminum chloride (DEAC) and triethylaluminum (TEAL) was found to be an effective catalyst for producing butadiene rubber (BR) with a high content of *cis* 1,4- configuration (> 97%) and low *vinyl*-1,2-configuration(< 1%). It was found that the increase in the Co content in the mixed Co/Nd catalyst to the molar ratio of from 0.0/1.0 to 0.3/0.7 or 0.4/0.6 enhanced the BD conversion from 68% to 73-74%. A high *cis*-1,4 configuration (>97%) with a low amount of both *trans*-1,4 (<2%) and *vinyl*-1,2 (<1%) units in the BR structure was obtained when the Co content in the mixed catalyst increased. This reflected a synergetic effect between Co and Nd in this mixed catalyst. The Mw and MWD of BR was found to decrease when the Co/Nd molar ratio increased due to the effect of the Co catalyst producing BR with high branching and low Mw.

To consider the effect of co-catalysts, an increase in the amount of the TEAL/Nd molar ratio increased the BD conversion due to the effect of TEAL acting as a moisture scavenger and impurities present in the polymerization process. In addition, an overdose of TEAL decreased the *cis*-1,4 and *vinyl*-1,2 configuration in the BR obtained (Co/Nd-BR). This could be explained in that TEAL was an electron donor, which could compete with the new incoming BD monomers to coordinate with the metal catalyst. In the case of DEAC, it was noticed that the suitable DEAC/Nd molar ratio for producing Co/Nd-BR with high BD conversion was less than 1.7. The excess chlorinating agent might induce the precipitation of the prepared catalyst to form insoluble particles of $NdCl_3$, which diminished the catalytic activity.

For the effect of the monomer concentration, the results indicated that a higher monomer concentration increased the BD conversion with a higher content of *cis*-1,4 configuration in the Co/Nd-BR to 97.5%.. Moreover, it was found that an increase in the reaction temperature increased the level of BD conversion and slightly promoted *cis-trans* isomerization to increase the amount of *trans*-1,4 units in the Co/Nd-BR. Above 55 ^{o}C, the BD conversion significantly decreased due to deactivation of the catalyst. For the effect of solvent, an increase in the amount of the cyclohexane portion in the mixed toluene/cyclohexane gave high BD conversion (ca. 90% BD conversion when using a pure cyclohexane).

To investigate the vulcanization and mechanical properties of Ni/Nd-BR, it was found that the Mooney viscosity, scorch time and optimum cure time of Co/Nd-BR gum was similar to that of commercial BR gums obtained from BD polymerization using Ni- and Nd-based catalyst systems. However, Co/Nd BR exhibited superior properties in terms of tensile strength, rebound and abrasion properties.

A kinetic study showed that the BD polymerization using a Co/Nd mixed catalyst followed a first order dependence on the BD concentration. The reaction rate increased on increasing the reaction temperature from 45-55 ^{o}C. Above 55 ^{o}C, the polymerization rate decreased due to deactivation of the catalyst. The apparent activation energy (Ea) for this catalyst system was calculated as 25.6 kJ/mol. This low value of Ea implied that this polymerization system was under a mass-transfer limitation.

6.1.3 1,3-Butadiene polymerization using Ni/Nd-based Ziegler-Natta catalyst

The BD polymerization using a Ni/Nd-based Ziegler-Natta catalyst at a Ni/Nd molar ratio of 0.3/0.7 coordinated with DEAC and TEAL at DEAC/Nd and TEAL/Nd molar ratios of 1.5/1.0 and 5.0/1.0, respectively in the presence of toluene resulted in ca. 75% BD conversion. The increasing Ni content in the Ni/Nd mixed catalyst decreased the BD conversion and produced BR (Ni/Nd-BR) with a lower amount of both *trans*-1,4 and *vinyl*-1,2 structures. When the amounts of TEAL and DEAC increased, both levels of *trans*-1,4 and *vinyl*-1,2 configurations in the obtained Ni/Nd-BR increased. The high BD conversion at 80% was achieved when the reaction temperature increased from 45 to 60 ^{o}C.

The BD polymerization catalyzed by the Ni/Nd-based catalyst using cyclohexane as a media provided 100% BD conversion and the obtained Ni/Nd-BR had a very low amount of *vinyl*-1,2 units (0.07%).

For the vulcanization and mechanical properties of Ni/Nd-BR, the results showed that a scorch time (ts_1) and an optimum cure time (tc_{90}) of the Ni/Nd-BR were similar to those of commercial Ni-BR and Nd-BR. This was due to a similar level of *cis*-1,4 configuration in all BRs. The Ni/Nd-BR had higher mechanical performance, such as tensile strength, elongation and hardness compared to the commercial BRs. This was attributed to the high content of *cis-1,4* and *trans*-1,4 configurations in the Ni/Nd-BR resulting from an influence of both Nd and Ni species in the Ni/Nd-based catalyst.

6.2 Recommendations

A further study of the effect of Co/Nd- and Ni/Nd-based Ziegler-Natta catalysts on BD polymerization should be concerned with the following aspects:

6.2.1 Ageing period and temperature of mixed catalyst solution

Since the ageing period and temperature of the studied catalyst systems were kept constant at 50 ^{o}C for1 h, the effect of the ageing period and temperature on the performance of these catalysts for BD polymerization in terms of BD conversion, microstructure and molar mass of BR will be required in further investigations.

6.2.2 Type of co-catalyst

Selection of co-catalyst type is one of the important factors for Ziegler-Natta based catalyst systems. Thus, the effect of co-catalyst type such as ethylaluminum sesquichloride (EASC), di-isobutylaluminum hydride (DIBAH) and triisobutylaluminum (TIBA) for the Ni/Nd- and Co/Nd-based catalyst systems should be further studied.

6.2.3 Molecular study of Ni/Nd- and Co/Nd-based catalysts

It is still unclear about the reasons for color change and the catalytic mechanism to form the active sites of the Ni/Nd- and Co/Nd-based catalysts. Since, the obtained experimented data for Co/Nd and Ni/Nd catalyst are insufficient to propose the mechanism of catalyst for BD polymerization, the more sophisticated experiments are required to characterize these mixed catalysts during BD polymerization.

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APPENDIX A
RUBBER PROPERTY

Table A-1 Properties of Commercial BRs.

Analysis items	Co-BR	Ni-BR	Nd-BR
1. Volatile matter	0.5	0.75	0.75 max
2. Mooney viscosity	38-48	40-50	44
3. ASH content	0.5 % max	0.5 % max	0.5 % max
4. Organic acid	-	-	1.0 % max
5. *Cis* 1,4 content	97 % min	95 % min	96 % min

APPENDIX B

CALCULATION OF MICROSTRUCTURE USING NMR

^{1}H-NMR calculation

The value of *cis*-1,4(c), t*rans*-1,4(t) and *vinyl*-1,2(v) were calculated through the formulas

$$c = (I_9 - 0.516) / (2I_1 + I_2) \qquad (1)$$

$$t = (I_4 - 0.515) / (2I_1 + I_2) \qquad (2)$$

$$v = I_2 / (I4-0.5I5) \qquad (3)$$

Where the values of integrated intensity were estimated as shown in Table B-1

Table B-1 Assignment of signals in the 1H NMR spectrum of polybutadiene.

Signals	Chemical shifts δ_H, ppm	Groups of carbon atoms
I_1	5.8-5.2	Olefinic proton of 1,2 units and protons at double bonds of 1,4 units
I_2	5.15-4.75	Vinylene protons of 1,2 units
I_3	2.40-2.05	Ethylene protons of 1,2 units (“intrablock”) and methylene protons of cis-1,4 units
I_4	2.05-1.80	Methylene protons of trans-1,4 units and methane protons of 1,2 additions (joint with 1,4 units)
I_5	1.55-1.40	Methylene protons of joint 1,2 units
I_6	1.4-1.2	Methylene protons of “intrablock” 1,2 units

^{13}C-NMR calculation

The values of *cis*-1,4(c), t*rans*-1,4(t) and *vinyl*-1,2(v) were calculated through the formulas

$$v = (I_7 + I_9) / (I_7 + I_8 + I_9) \qquad (4)$$

$$t = (I_{10} - I_7 - I_9 + I_{12} + I_{14}) / (I_7 + I_8 + I_9) \qquad (5)$$

$$c = (I_{11} + I_{13} + I_{15}) / (I_7 + I_8 + I_9), \qquad (6)$$

Where the values of integrated intensity were estimated as shown in Table B-2

Table B-2 Assignment of signals in the 13C NMR spectrum of polybutadiene.

Signals	Chemical shifts δ_H,ppm	Groups of carbon atoms
I_7	145-141	Vinylene carbon V_3 or 1,2 units
I_8	134-126	Olefinic carbon T_2 and C_2 of 1,4 units
I_9	116-112	Vinylene carbon V_4 or 1,2 units
I_{10}	46.0-33.8	Carbons V_1 and V_2 of 1,2 units and carbon T_1 or *trans*-1,4 units in the combinations v_2T_1 …*c/t/v*$_2$ and vv_2T_1
I_{11}, I_{13} ,I_{15}	33.8-33.2,32.4-31.0,29-22	Methylene carbons C_1 of cis-1,4-units
I_{12}	33.2-32.4	Methylene carbons T_1 trans-1,4-units and cis-1,4-units (in combination v_2C1…*c/t*)
I_{14}	31.29	Methylene carbons $T_1$of trans-1,4-units

Table B-3 Microstructure using FT-IR, ^{1}H NMR and ^{13}C NMR.

	Microstructure (%)	FT-IR	^{1}H- NMR	^{13}C -NMR
Co-BR	*Cis*-1,4	98.0	97.7	97.7
	Trans-1,4	0.81	0.25	1.45
	Vinyl-1,2	1.19	2.05	0.88
Nd-BR	*Cis*-1,4	97.6	98.9	95.0
	Trans-1,4	2.12	0.12	4.40
	Vinyl-1,2	0.28	0.98	0.60
(Co/Nd)-BR	*Cis*-1,4	98.2	99.3	97.2
	Trans-1,4	1.40	-	2.80
	Vinyl-1,2	0.40	0.70	-

APPENDIX C

RAW DATA WITH STANDARD DEVIATION

Table C-1 Effect of Co/Nd molar ratio on %conversion, microstructure and physical properties of BR gum.

Co/Nd	Conversion (%)	Microstructure (%)			Mw (x 10^5)	MWD
		Cis-1,4	*Trans*-1,4	*Vinyl*-1,2		
0.0/1.0	67.7±0.07	96.3±0.06	2.83±0.08	0.87±0.01	8.25±0.12	2.5±0.16
0.2/0.8	64.2±0.28	97.2±0.45	1.99±0.44	0.77±0.02	8.31±0.87	2.3±0.11
0.3/0.7	73.1±1.15	96.9±0.15	2.27±0.15	0.83±0.01	7.94±1.01	2.3±0.14
0.4/0.6	74.1±0.99	96.9±0.13	2.42±0.11	0.72±0.01	6.61±0.75	2.4±0.01
0.5/0.5	27.5±2.20	97.7±0.28	1.57±0.17	0.73±0.11	7.33±0.08	3.4±0.55
1.0/0.0	0	0	0	0	0	0

Table C-2 Effect of TEAL/Nd ratio on %conversion, microstructure and physical properties of BR gum.

TEAL/Nd	Conversion (%)	Microstructure (%)			Mw (x 10^5)	MWD
		Cis-1,4	*Trans*-1,4	*Vinyl*-1,2		
3.0/1.0	0	0	0	0	0	0
5.0/1.0	73.1±1.15	96.9±0.15	2.27±0.15	0.87±0.01	7.94±0.01	2.3±0.14
7.0/1.0	82.0±1.73	96.0±0.57	3.34±0.26	0.84±0.04	5.35±0.09	2.7±0.05
9.5/1.0	81.5	94.8	4.38	0.82	4.71	3.0

Table C-3 Effect of polymerization temperature on % conversion, microstructure and physical properties of BR gum.

	Conversion	Microstructure (%)			Mw	MWD
	(%)	*Cis*-1,4	*Trans*-1,4	*Vinyl*-1,2	(x $10^{5)}$	
45	66.9	97.7	2.11	0.19	8.56	2.5
50	73.1±1.15	96.9±0.15	2.27±0.15	0.83±0.01	7.94±0.01	2.3±0.14
55	81.8±2.62	97.0±0.15	2.43±0.04	0.57±0.07	7.53±0.58	2.6±0.41
60	56.9±1.22	96.5±0.12	2.69±0.08	0.84±0.04	6.86±1.23	3.0±0.18

Table C-4 Effect of BD concentration on % conversion, microstructure, Mw and MWD of Co/Nd)-BR gum.

BD	Conversion	Microstructure (%)			Mw	MWD
(%w/w)	(%)	*Cis*-1,4	*Trans*-1,4	*Vinyl*-1,2	(x 10^{5})	
2.53	73.6±0.24	96.6±0.25	2.75±0.10	0.65±0.16	7.08±0.37	2.5±0.25
3.01	73.1±1.15	96.9±0.15	2.27±0.15	0.83±0.01	7.94±0.01	2.3±0.14
3.31	80.6±0.04	97.5±0.02	1.75±0.06	0.75±0.05	9.84±0.08	2.7±0.15

APPENDIX D

APPARENT ACTIVATION ENERGY

The apparent activation energy is calculated using Arrhenius equation as follows

$$k = f(T) = A\, e^{-E/RT}$$

Where T is the absolute temperature, E is the activation energy (Ea) and R is the universal gas constant= 1.98 cal K^{-1} mol^{-1}

The polymerization reaction was carried out at 45, 50 and 55 ºC at constant catalyst and monomer concentrations. The rate constant (k) at different temperature is obtained from the slope of plotting between reaction rate and time as shown in Figure 4.10. The rate constant values were shown in Table D-1. The activation energy is calculated by plotting of log k and 1/T as demonstrated in Figure D-1. The slope of line shows -1334.9 (-E/2.3R). Thus, the 25.6 kJ/mole of apparent activation energy is obtained from this calculation.

Table D-1 Effect of temperature on reaction rate.

Temperature(K)	k(s-1)	1/T	log k
318	0.0137	0.003145	-1.8633
323	0.0155	0.003096	-1.8097
328	0.0184	0.003049	-1.7351

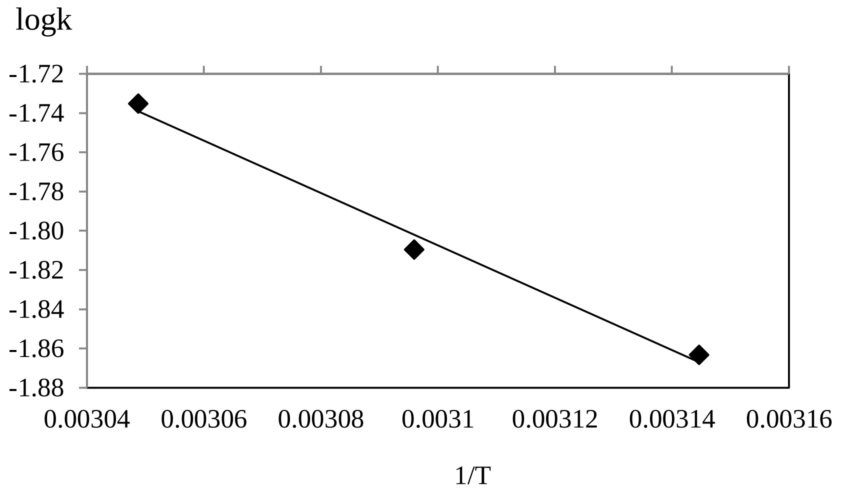

Figure D-1 Plot of log k as a function of temperature

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Journal Publication

C. Chatarsa, P. Prasassarakich, G.L. Rempel, N. Hinchiranan. Polymerization of 1,3-Butadiene using Co/Nd-Based Ziegler/Natta Catalyst: Microstructure and Physical Properties. Polymer Engineering & Science Journal, 2014, DOI 10.1002/pen. 23864

Conference Presentation

C. Chatarsa, P. Prasassarakich, G.L. Rempel, N. Hinchirana. "Production of Butadiene Rubber with High Cis-1,4-Configuration using Co/Nd-based Ziegler/Natta Catalyst" poster presentation conference on 23rd North American Catalysis Society Meeting, 2-7 June 2013 in Louisville, Kentucky, USA.