

# **Stereospecific Polymerization of 1, 3-butadiene in an Environment Friendly Solvent: Kinetic Studies**

By

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08MCH004



**DEPARTMENT OF CHEMICAL ENGINEERING  
INSTITUTE OF TECHNOLOGY  
NIRMA UNIVERSITY  
AHMEDABAD-382481**

May 2010

# **Stereospecific Polymerization of 1, 3-butadiene in an Environment Friendly Solvent: Kinetic Studies**

**Major Project**

Submitted in partial fulfillment of the requirements

For the degree of

**Master of Technology in Chemical Engineering (EPD)**

By

**Archana Singh**

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**AHMEDABAD-382481**

**May 2010**

## Declaration

This is to certify that

- i) The thesis comprises my original work towards the degree of Master of Technology in Chemical Engineering (EPD) at Nirma University and has not been submitted elsewhere for a degree.
- ii) Due acknowledgement has been made in the text to all other material used.

**Archana Singh**

## Certificate

This is to certify that the Major Project entitled "Stereospecific Polymerization of 1, 3-butadiene in an Environment Friendly Solvent: Kinetic Studies " submitted by Archana Singh (08MCH004), towards the partial fulfillment of the requirements for the degree of Master of Technology in Chemical Engineering (EPD) of Nirma University, Ahmedabad is the record of work carried out by him under my supervision and guidance. In my opinion, the submitted work has reached a level required for being accepted for examination. The results embodied in this major project, to the best of my knowledge, haven't been submitted to any other university or institution for award of any degree or diploma.

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## Abstract

In PBR-II plant of RIL-VMD, polybutadiene is manufactured using nickel based catalyst system consisting of nickel naphthenate [catalyst], boron trifluoride etherate [promoter], triethylaluminium [co-catalyst]. The detailed kinetic data of the reaction were not provided by the licensor of PBR-II plant. Moreover, the kinetics of nickel based system is not readily available in the open literature. Hence, in this work, effect of nickel based Ziegler-Natta catalyst system on polymerization of 1, 3- butadiene and its detailed kinetics in an environment friendly solvent system (toluene: heptane 50:50) was studied. And it was found that ratio of promoter to co-catalyst is one of important parameters governing the polymerization. Polymerization is 1st order with respect to monomer concentration as well as catalyst concentration in case of both the catalyst systems. The overall rate constant was found to be  $1.462 \text{ min}^{-1}\text{mol}^{-1}$  for nickel based catalyst system. The activation energy of the polymerization based on this catalyst system was found to be  $14.5\text{kcal mol}^{-1}$ .

Besides, PBR-I plant of RIL-VMD utilizes benzene as the solvent for the polymerization of 1, 3-butadiene using cobalt based catalyst system. The cobalt catalyst system comprises of cobalt octanoate [catalyst], diethylaluminium chloride [co-catalyst] and water [promoter]. Benzene is a carcinogenic solvent which leads to Hematoxin that is linked to increased incidence of leukaemia in humans. So, in this study an attempt was taken to study the 1, 3-butadiene polymerization kinetics in non-carcinogenic cyclohexane solvent so that plant could be benefited while changing over the existing solvent to non-carcinogenic one. From this study, the following conclusions can be made. Polymerization is 1st order with respect to monomer concentration as well as catalyst concentration. The overall rate constant was found to be  $0.68 \text{ min}^{-1}\text{mol}^{-1}$  for cobalt based catalyst system. The activation energy of the polymerization based on this catalyst system was found to be  $13.7\text{kcal mol}^{-1}$ .

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08MCH004

# Contents

Declaration	iii
Certificate	iv
Abstract	v
Acknowledgements	vi
List of Tables	ix
List of Figures	x
<b>1 Introduction</b>	<b>2</b>
1.1 Preliminary Remarks . . . . .	2
1.2 Major Producers of cis 1, 4-Butadiene Rubber . . . . .	4
1.3 Historical Background . . . . .	5
1.4 Types of polybutadiene rubber . . . . .	6
1.4.1 Cis- polybutadiene . . . . .	6
1.4.2 Trans Polybutadiene . . . . .	8
1.5 Manufacturing Process of Polybutadiene rubber . . . . .	8
1.6 Properties of butadiene rubber . . . . .	10
1.7 Major Applications of Polybutadiene . . . . .	10
<b>2 Literature Review</b>	<b>12</b>
2.1 Background . . . . .	12
2.2 Literature Review . . . . .	13
2.3 Scope and Objectives . . . . .	18
<b>3 Experimental</b>	<b>20</b>
3.1 Materials . . . . .	20
3.1.1 Monomer . . . . .	20
3.1.2 Solvents . . . . .	20
3.1.3 Catalysts . . . . .	20
3.1.4 Carbon Disulfide ( $CS_2$ ) . . . . .	21

3.1.5	Short-stop . . . . .	21
3.1.6	Antioxidant: Di-tertiary butyl p-cresol (DTBPC) . . . . .	21
3.2	Preparation of Feed . . . . .	21
3.3	Polymerization . . . . .	22
3.3.1	Nickel based catalyst system . . . . .	22
3.3.2	Cobalt Based catalyst system . . . . .	22
3.4	Polymer Recovery . . . . .	23
3.5	Sample Drying . . . . .	23
3.6	Sample Drying . . . . .	23
3.7	Conversion . . . . .	24
3.8	Microstructure . . . . .	24
3.9	Gel-permeation chromatography . . . . .	24
3.10	Safety precautions . . . . .	24
<b>4</b>	<b>Results And Discussion</b>	<b>25</b>
4.1	Effect of catalyst ageing on polymerization of 1, 3-butadiene . . . . .	26
4.2	Effect of BRF/TEAL ratio on polymerization of 1, 3-butadiene . . . . .	27
4.3	Effect of catalyst (NIC) concentration on polymerization of 1, 3-butadiene . . . . .	29
4.4	Effect of catalyst (NIC) concentration on polymerization of 1, 3-butadiene . . . . .	30
4.5	Characterization of the polymers . . . . .	30
4.6	Kinetic Studies . . . . .	34
4.7	Kinetics studies . . . . .	41
<b>5</b>	<b>Conclusion</b>	<b>50</b>
<b>6</b>	<b>Scope for further work</b>	<b>52</b>
	<b>References</b>	<b>54</b>



# List of Tables

I	Major producers of cis 1, 4-Butadiene Rubber . . . . .	4
II	Major Applications of different polybutadienes . . . . .	11
I	Comparison of PBR-I and PBR-II Plants of RIL-VMD . . . . .	13
I	Effect of catalyst ageing on characteristics of rubber . . . . .	26
II	Effect of BRF/TEAL ratio on conversion . . . . .	28
III	Effect of catalyst (NIC) concentration on conversion . . . . .	29
IV	Microstructure of different polymers . . . . .	32
V	Polymer conversion at various monomer concentrations at constant catalyst concentration and temperature . . . . .	36
VI	Effect of temperature on reaction rate . . . . .	40
VII	Polymer conversion at various monomer concentrations at constant catalyst concentration and temperature . . . . .	43
VIII	Effect of temperature on reaction rate . . . . .	49

# List of Figures

1.1	World Consumption Pattern of Butadiene Rubber (2007)	3
1.2	Chemical structure of High cis Polybutadiene rubber	7
1.3	Chemical structure of vinyl Polybutadiene rubber	8
1.4	Chemical structure of High trans Polybutadiene rubber	8
1.5	Chemical structure of 1, 3-butadiene monomer	9
1.6	Schematic description of polymerization of 1, 3- butadiene	9
3.1	Feed preparation assembly	22
3.2	1, 3 Butadiene Polymerization Assembly (Buchi Diagram)	23
4.1	Mechanism of polymerization	26
4.2	Effect of ageing temperature on conversion	27
4.3	Plot of BRF/TEAL vs. conversion	28
4.4	Plot of catalyst concentration vs. conversion	29
4.5	Plot of monomer concentration vs. conversion	30
4.6	Effect of conversion on Mw and PDI of the polymer	31
4.7	Effect of catalyst concentration on Mw and PDI	31
4.8	Effect of temperature on Mw and PDI	32
4.9	Effect of polymerization [a] time and [b] temperature on density of the elastomer	33
4.10	Effect of catalyst concentration on density of the elastomer	33
4.11	Course of the conversion as a function of time	34
4.12	1 <sup>st</sup> order plot of the polymerization [at monomer concentration 1.8mol/l]	37
4.13	1 <sup>st</sup> order plot of the polymerization [at monomer concentration 2.64mol/l]	37
4.14	1 <sup>st</sup> order plot of the polymerization [at monomer concentration 2.96mol/l]	38
4.15	1st order plot of the polymerization of butadiene, at monomer concentration= 2.64mol/l, and at catalyst concentration of ◦ 2.8 mmphgm,△ 3.8 mmphgm and ◻ 4.8 mmphgm	38
4.16	Plot of k as a function of catalyst concentration	39
4.17	Effect of temperature on reaction rate	40
4.18	Plot of log k vs. 1/T	41
4.19	Mechanism of in-situ generation of different Lewis acidity from the reaction of DEAC and water and its effect on polymerization	41

4.20	Course of the conversion as a function of time . . . . .	42
4.21	1 <sup>st</sup> order plot of the polymerization [at monomer concentration 1.29mol/l]	44
4.22	1 <sup>st</sup> order plot of the polymerization [at monomer concentration 1.85mol/l]	44
4.23	1 <sup>st</sup> order plot of the polymerization [at monomer concentration 2.59mol/l]	45
4.24	1 <sup>st</sup> order plot of the polymerization of butadiene, at monomer concentration= 2.59mol/l, and at catalyst concentration 0.01mmphgm . . .	45
4.25	1 <sup>st</sup> order plot of the polymerization of butadiene, at monomer concentration= 2.59mol/l, and at catalyst concentration 0.02mmphgm . . .	46
4.26	1 <sup>st</sup> order plot of the polymerization of butadiene, at monomer concentration= 2.59mol/l, and at catalyst concentration 0.03mmphgm . . .	46
4.27	Plot of k as a function of catalyst concentration . . . . .	47
4.28	Effect of temperature on reaction rate at 10°C . . . . .	47
4.29	Effect of temperature on reaction rate at 20°C . . . . .	48
4.30	Effect of temperature on reaction rate at 25°C . . . . .	48
4.31	Plot of log k vs. 1/T . . . . .	49

# Chapter 1

## Introduction

### 1.1 Preliminary Remarks

Butadiene rubber (BR) is the second largest volume synthetic rubber produced, next to styrene-butadiene rubber (SBR). Consumption of BR is about 25, 00, 000 tons worldwide presently Fig.1 shows the world consumption pattern of butadiene rubber in 2007. Currently, automobile tires are the primary application for BR, a market segment responsible for 67-70% of the world's BR production consumption.

Four different technologies with Ziegler-Natta catalysts can be used in the commercial production of BR with high 1, 4-cis repeating unit levels; titanium (Ti), cobalt (Co), nickel (Ni), and neodymium (Nd) are the most commonly used metals in these catalyst systems[1].

BR is commercially available in two main forms: one containing 1, 4-cis repeating unit levels around 40%, which is called low-cis BR, and one with levels that range from 92 to 98%, called high-cis BR. The demand for these two products, each with its own distinct properties, comes from major consumption segments, tires and retreads, with high-cis BR being the most appropriate for these applications.[1]

Cured BR imparts excellent abrasion resistance (good tread wear), and low rolling resistance (good fuel economy) due to its low glass transition temperature (Tg). The

low  $T_g$ , typically  $< -90$  deg C, is a result of the low vinyl content of BR. However, low  $T_g$  also leads to poor wet traction properties, so BR is usually blended with other elastomers like natural rubber (NR) or SBR for tread compounds. A second segment is that of plastic modification, which accounts for 15-20% of the BR production worldwide; the footwear, technical goods, and golf ball segments consume 5-20% of this elastomer's worldwide production [1]. Typically about 7% BR is added to the polymerization process to make these rubber-toughened resins such as high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene resin (ABS).

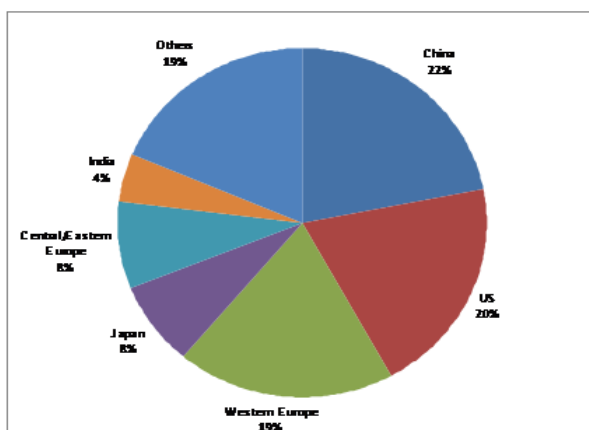


Figure 1.1: World Consumption Pattern of Butadiene Rubber (2007)

## 1.2 Major Producers of cis 1, 4-Butadiene Rubber

Table I: Major producers of cis 1, 4-Butadiene Rubber

Catalyst	Producer companies
Cobalt	Lanxess Nippon Zeon American Synthetic Rubber corp. [Michelin] UBE Industries Ltd. Taiwan Synthetic Rubber Corporation. Dow Ashahi TSRC Corp., Taiwan <b>Reliance Industries Ltd., India</b> Korea Kumho, Korea BST Elastomer, Bangkok Polimeri (Enichem Elastomeri )S.r.l. Michelin et CIE Kumho Petrochemical Co.,Ltd LG Chemical Petkim, Turkey PETROFLEX-Industria e Comercio, Brazil SINO PEC, China Thai Synthetic Rubber, Thailand

Nickel	Goodyear Tyre and Rubber Co. Ltd Japan Synthetic Rubber Co. Ltd. <b>Reliance Industries Ltd., India</b> Firestone Polymers BST Elastomer, Bangkok
Lithium	Lanxess Nippon Zeon Polimeri Europa Dow Chi Mei Corporation, Taiwan Firestone Polymers
Neodymium	Polimeri Europa Lanxess JSR, Japan Korea Kumho, Korea Petro China, China Karbochem, S. Africa Sibur, Russia Chi Mei Corporation Firestone Polymers Nizhnekamskneftekhim, Russia Voronezh Syntezkauchuk, Russia

### 1.3 Historical Background

Polybutadiene for the first time was prepared by Lebdev, a Russian in 1910 by using alkali metals as the initiator in diene polymerization. His work eventually led to the first industrial production facility. During the 1920's and 1930's emulsion polymerization process was developed for SBR. Despite the arduous efforts, emulsion polymerized BR was not accepted as a large scale commercial prospect in 1940's. Development of stereospecific catalyst system in mid 1950's marked a significant development in BR manufacturing [2].

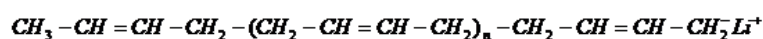
The first production run of high-cis BR came off the line in 1960 under the responsibility of Phillips Petroleum Co. with a titanium-based catalyst. Still in the 1960s, high-cis BR started to be produced with cobalt based catalysts. Goodrich-Gulf was the first company to market this polymer. Bridgestone Tire Co., together with Japan

Synthetic Rubber Co., developed the production of this polymer with a nickel-based catalyst, which was marketed in Japan in 1964 by Japan Synthetic Rubber. In that same decade, studies on neodymium- based catalyst systems started to be carried out; however, only in the 1980s they started to be commercially used by Enichem to produce high-cis BR. Before high-cis BR produced with neodymium-based catalysts currently the one of greater commercial interest, began to be marketed, the cobalt-based catalysts were the most extensively studied due to the technological and commercial advantages of these systems [1].

## 1.4 Types of polybutadiene rubber

### 1.4.1 Cis- polybutadiene

- a. Low Cis:: The alkyllithium or "anionic" catalyst system produces a polymer with about 40% cis, 50% trans and 10% vinyl. The alkyllithium process is probably the most versatile, because the growing chain end contains a "living" anion (negative charge) which can be further reacted with coupling agents or functional groups to make a variety of modified polybutadienes. It also produces gel-free polybutadiene making it ideal for plastics modification. Vinyl increases the Tg of the polybutadiene by creating a stiffer chain structure. Vinyl also tends to crosslink or "cure" under high heat conditions so the high vinyl polymers are less thermally stable than low vinyl. Vinyl units can be increased in lithium-based anionic polymerisation through the use of polar modifiers, which are usually nitrogen or oxygen-containing compounds. The modifiers direct the attack of the propagating anion on the "living" chain end to give a 1,2 addition to the butadiene monomer. Growing "living" anion (negative charge) on end of live polybutadiene chain with Lithium counterion (positive charge) [3] is shown below :





- b. High Cis : The transition metal, or so called Ziegler- Natta catalysts produce very "stereoregular" polybutadienes with one type having the main polymer chain on the same side of the carbon-carbon double bond contained in the polybutadiene backbone. This is called high cis polybutadiene rubber.

The neodymium catalyst system produces the highest cis content of about

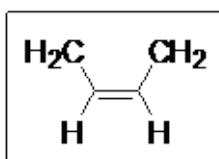


Figure 1.2: Chemical structure of High cis Polybutadiene rubber

99% and also makes the most linear chain structure (no branching) producing a polymer with the best tensile and hysteresis (low heat build-up) properties of all the high cis types. The cobalt system produces a highly branched BR with a low solution viscosity that makes a good polystyrene and acrylonitrile-butadiene-styrene modifier. The nickel catalyst makes polybutadiene with an intermediate level of branching.[3]

High cis polybutadiene will usually have cis content  $>95\%$  , trans (Fig.1.3) content is less than 2% and vinyl content (Fig.1.3) is less than 1% which gives rise to better "green strength" and increased cut growth resistance in the cured product. Green strength, which is the strength of the uncured rubber compound, is important for the tyre building process and cut growth resistance is necessary for tyre performance. High cis polybutadiene also shows lower Tg compared to alkyllithium-based BR because it has almost no vinyl structure. vinyl tends to increase the Tg of the polymer. The low vinyl content and low Tg makes high cis polybutadiene ideal for golf ball cores. Golf ball cores are cured with peroxides, which tend to "over cure" the vinyl units making a very hard and slow golf ball.

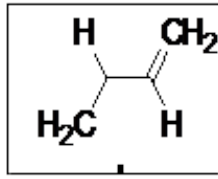


Figure 1.3: Chemical structure of vinyl Polybutadiene rubber

### 1.4.2 Trans Polybutadiene

In the trans configuration the main polymer chain is on opposite sides of the internal carbon-carbon double bond. Trans polybutadiene has a melting point of about 80C. It is made with transition metal catalysts similar to the high cis process (La, Nd, and Ni). These catalysts can make polymers with >90% trans again using the solution process.(Fig.1.4)

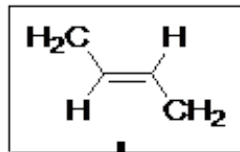


Figure 1.4: Chemical structure of High trans Polybutadiene rubber

## 1.5 Manufacturing Process of Polybutadiene rubber

Most polybutadienes are made by a solution process, using either a transition metal (Nd, Ni, or Co) complex or an alkyl metal, like butyllithium, as catalyst. Since the reaction is very exothermic, and can be explosive, particularly with alkyllithium catalysts, the reaction is normally carried out in solvents like hexane, cyclohexane, benzene or toluene. The solvents are used to reduce the rate of reaction, control the heat generated by the polymerisation and to lower the viscosity of the polymer solution in the reactor. A typical polybutadiene polymerisation would be run at about 20% monomer and 80% solvent [3].

Polybutadiene is a homopolymer (only one monomer) of 1, 3 butadiene, a monomer containing four carbon atoms, and six hydrogen atoms ( $C_4H_6$ ). The four carbon atoms are in a straight chain containing two "double bonds" as follows : (Fig.1.5). The polymerization of 1, 3-butadiene is shown in Fig. 1.6 [3].

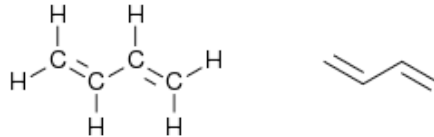


Figure 1.5: Chemical structure of 1, 3-butadiene monomer

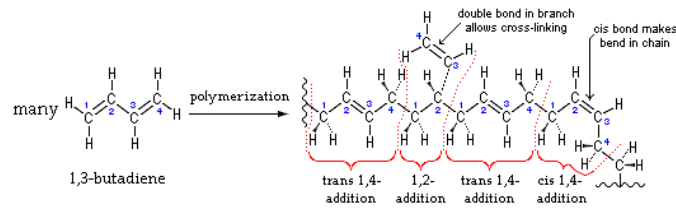


Figure 1.6: Schematic description of polymerization of 1, 3- butadiene

It is the double bonds that are the key to polymer formation. They are attacked by catalysts to maintain a repetitive chain growth process which continues until something is added to terminate the reaction at the desired molecular weight. The polymerization can either be a batch process or a continuous process. In batch mode, monomer, solvent and catalyst are charged to the reactor, heated to initiate the process, and then allowed to continue to completion. The polymer solution is then transferred to another vessel or process unit to remove the solvent. In continuous mode, monomer, solvent and catalyst are continuously fed into the bottom of the first of a series of reactors at a temperature suitable for polymerization. The polymerization progresses as the solution flows through the reactors and polymer solution is taken off at the top of the last reactor without stopping the process. The continuous process is the most economical. [3]

## 1.6 Properties of butadiene rubber

The properties of vulcanized high cis-BR are summarized below :

- a. Vulcanized high-cis BR presents high elasticity and resilience.
- b. Low heat buildup.
- c. High resistance to abrasion and to cut growth.
- d. Good flexibility in low temperatures, and high fatigue cracking resistance.
- e. It can take a higher level of carbon black and oil compared to natural rubber (NR).
- f. On the other hand, its compositions have low skidding resistance and with low resistance to heat and ozone,. For this reason, high-cis BR is always used in mixtures with other polymers, especially SBR and NR; this mixing enhances some of the properties of vulcanized articles made of these elastomers [1].

## 1.7 Major Applications of Polybutadiene

Major applications of different polybutadienes rubber[4] are listed in Table II:

The uses of high-cis BR are summarized as follows :

- Polybutadiene is largely used in various parts of automobile tires. Its use in the tread portion of giant truck tires helps to improve the abrasion, i.e. less wearing, and to run the tire comparatively cool, since the internal heat comes out quickly.
- In the sidewall of truck tires, the use of polybutadiene rubber helps to improve fatigue to failure life due to the continuous flexing during run. As a result, tires will not blow out in extreme service conditions.

- In the carcass, this rubber may not be used, due to poor adhesion.
- Polybutadiene rubber may be used in the inner tube of hoses for sandblasting, along with natural rubber. The main idea is to increase resilience. This rubber can also be used in the cover of hoses, mainly pneumatic and water hoses.
- This rubber can also be used in railway pads, bridge blocks, golf balls, footwear, for HIPS production etc.
- This rubber can also be used in railway pads, bridge blocks, golf balls, footwear, for HIPS production etc.
- In car tires, polybutadiene rubber can be used with SBR in the tread portion.
- Polybutadiene rubber can be blended with nitrile rubber for easy processing. However large use may affect oil resistance of nitrile rubber.
- High cis liquid polybutadiene is used in Surface coating (aqueous solvent.), Adhesives, Thermosetting resin formulations, synthetic drying oils.

Table II: Major Applications of different polybutadienes

<b>High cis 1,4</b>	<b>High trans 1,4</b>	<b>High syndio-tactic 1,2</b>	<b>High cis liquid PB</b>
1. Tire and related products 2. Truck tire tread 3. Side wall 4. Car carcass 5. Rethreading materials 6. V-belts 7. Battery boxes 8. Plastic modifications 9. Blend with NR, SBR, IR	Sports goods	1. As a new thermoplastic films and fibers 2. carbon fibers 3. Graphite fibers	1. Surface coating (aqueous solvent) 2. Adhesives 3. Thermosetting resin formulations 4. As synthetic drying oils

# Chapter 2

## Literature Review

### 2.1 Background

In 1978, IPCL Vadodara, now Reliance Industries Ltd-Vadodara Manufacturing Division (RIL-VMD) set up PBR-I manufacturing facility with the know-how from Polysar Canada. The installed capacity of this plant was 20,000 TPA. Later in 1996, IPCL (RIL-VMD) set up another plant with the know-how from Japan Synthetic Rubber Co. Ltd., Japan. The installed capacity of this plant was 40,000 TPA. Both the plants use different solvent and catalyst systems. Table 2.1 compares the PBR-I and PBR-II plants of RIL-VMD, Vadodara.

Table I: Comparison of PBR-I and PBR-II Plants of RIL-VMD

Sr. No.	Subject	PBR-I	PBR-II
1.	Technology	M / S Polysar Canada (1978)	M / S Japan Synthetic Rubber (1996)
2.	Capacity	27 KTPA	43 KTPA
3.	Catalyst	Cobalt Octoate	Nickel Naphthenate
4.	Co-Catalyst	Diethylaluminium chloride ( $Et_2AlCl$ )	Triethylaluminium ( $Et_3Al$ )
5.	Promoter	Water, $H_2O$	Boron trifluoride etherate $BF_3.Et_2O$
6.	Solvent system	Benzene-Butene (70 / 30)	Toluene-Heptane (50 / 50)
7.	Temperature	24 – 29 °C	65 – 70 °C
8.	Chain Transfer Agent	1, 2 Butadiene	—
9.	Short Stop (Terminator)	Methanol	PPA (Phosphate of Polyoxyethylene alkyl phenyl ether)
10.	Anti-oxidant	Ditertbutyl-p-cresol DTBPC	DTBPC
11.	Reaction Time	60 – 65 min	4 hrs
12.	No of Reactors	3	4
13.	Feed Direction	Top – Bottom	Bottom – Top (Overflow)
14.	Conversion	60 to 65 %	~ 90 %
15.	Cis Content	> 96 %	> 96 %
16.	Gel Content	< 500 ppm	< 300 ppm
17.	Molecular weight distribution	2.5-3.5	3.0-4.0

## 2.2 Literature Review

Four different technologies with Ziegler-Natta catalysts can be used in the commercial production of BR with high 1, 4-cis repeating unit levels; titanium (Ti), cobalt (Co), nickel (Ni), and neodymium (Nd) are the most commonly used metals in these catalyst systems[1].

The Diethyl Aluminum Chloride (DEAC) in combination with cobalt catalysts requires water in a certain mole ratio to the DEAC to activate them as a catalyst to get 1, 4-cis structure. Catalyst has been found active when Water/ Aluminum (W/Al) ratio is varied in certain range [5].

Saltman and Kuzma in their report for the comparison between nickel and cobalt based catalyst systems, predicted that when nickel was used in recipes which gave solid polybutadienes of high molecular weight. With cobalt, only very low molecular weight liquid polybutadienes were obtained. When water activated cobalt catalyst is added to analogous nickel systems, only slight more viscous liquid polymers result [6].

Medvedev pointed out the predominant role of water, when it is absent 1,3 butadiene (BD) forms oligomers, using monochlorodiisobutyl aluminium and alcoholic complex of cobalt chloride under the given condition, rate of polymerization increases with concentration of cobalt and aluminium compound and varies in a strange way when water concentration changes.[7]

Hsu and Ng showed in study that the rate of polymerization in aromatic solvents shows a first order dependence on cobalt and monomer concentration [8]. Similarly both deactivation of catalyst and the chain transfer reaction have been of great importance on conversions and molecular weight. In support to Gippin they proved these results only by changing two pyridine compounds in their catalyst system [9]. Gippin used mixtures of benzene-hexane for his study using alkylaluminium and cobalt chloride as catalyst and concluded that the rate of polymerization is linear with respect to time in the initial stages and is a first order reaction with respect to monomer at fixed concentration of catalyst [10].

Gaylord et al. presented the Kinetic studies for polymerization of butadiene with aluminium trisobutyl titanium tetrachloride catalyst system in presence of heptane and they showed that the rate of disappearance of butadiene is dependent upon the molar ratio of the two catalyst components and the total concentration of the catalyst system [11].



The kinetics of polymerization of butadiene with catalyst prepared from some aluminum hydride derivatives,  $AlI_3, TiCl_4$  was investigated by Mazzei et al. and it was found that the reaction rate were 1st order with respect to monomer and catalyst concentration.[12]

Honig et al. studied the complex kinetics of cobalt based catalyst system in toluene as solvent by varying monomer and catalyst concentration. They established molecular weight relationship as a function of conversion, indicates that changes in molecular weight development occur at high conversions [13].

Hsu and Ng found that at a given W/Al ratio the rate was proportional to the square root of aluminium concentration. Conversion rate dependence on water level can be fitted by a half order equation i.e. by  $(W/Al)^{1/2}$  Rate =  $(W/Al)(CoCl_2)$  [2.1][8]

Marechal et al. reported the use of bis( $\pi$ -allyl) nickel trifluoroacetate for the polymerization of 1,3-butadiene in benzene which they found to be 1st-order reaction on monomer and catalyst.[14]

The catalytic behavior of the nickel stearate-diethyl aluminum chloride (DEAC) system in the polymerization of butadiene in toluene was discussed by Lee and Hsu. It was found that the overall rate of polymerization decreases with time but approaches a constant rate after about 10-30 min of reaction time depending on the relative amounts of the catalyst components. The propagation reaction was found to be first order with respect to monomer concentration. No appreciable termination reaction was observed [15].

Deb Nath et al. reported the kinetics of ziegler Natta polymerization of 1, 3-butadiene with a CoX<sub>2</sub>-MAO catalytic system and it was found to be 1st order with respect to monomer concentration.[16] The overall kinetic scheme for this process was:  $dm/dt = k_p[M][C^*]$

Where  $[C^*]$  is the concentration of active complexes.  $[M]$  molar concentration of monomer.

A kinetic modeling study was conducted for the Zeigler-Natta polymerization of BD with cobalt octanoate /DEAC/water catalyst by Lee et al. The model equations

for the single and dual site models were analytically solved and the closed form expressions for conversions of both number and weight average molecular weight were obtained [17].

Yoshimoto et al. investigated the effects of polymerization time, catalyst concentration, monomer concentration and polymerization temperature on the rate of polymerization and the molecular weight and the microstructure of the polymer. The rate equation used is:  $-d[M]/dt = aK_p[C]o[M]$  It was found that the rate of polymerization was first order with respect to monomer concentration and catalyst concentration.[18]

A numbers of organic compounds are reported in the literature as the chain transfer agents for such polymerizations (CTA). Examples are water, hydrogen, ethylene, propylene, alpha-olefins, allene, cyclooctadienes, cyclohexadienes, imides, ketones, alcohols, esters, nitriles, alkyl and alkenyl halides, thiophene, triethylamine and anisole [8].

The preferred solvents for 1, 3-butadiene polymerization are benzene or toluene. There are other solvents like heptane and cyclohexane which are also reported in literature. Advantage of using aromatic solvent is that they keep the polymer and catalyst in soluble form [5]

The nature of solvents employed in polymerization plays a definitive role in determining the polymerization rate, polymer molecular weight and its microstructure. Most of the laboratory polymerization studies of 1, 3-butadiene are done with single solvent where as industrial plant polymerization are performed in mixed solvents. Typically, a mixture of benzene and low boiling olefins are employed for this purpose [19].

Natta and Porri have reported that the rate of polymerization depends on aromatic solvent used and decreases in order: Benzene >Toluene >Xylene >Mesitylene [20]. Dielectric constant of the solvent has no effect on polymer cis content of the rubber. However, conversion decreases with increasing solvent dielectric constant [21]. Chandran et al. reported that cobalt salicylaldehyde complexes with ethyl aluminium sesquichloride (EAS) formed highly active butadiene polymerization catalysts, and

these complexes yield highly cis-1, 4-polybutadiene (>94%) with negligible amounts of 1, 4-trans. They also showed that the cis-content and weight average molecular weight decreases as polymerization temperature increased and also the yield and cis-content depends on butadiene concentration [22].

L. Porri et al. in his pioneered work showed that the cobalt containing catalyst prepared from alkyl aluminium compounds containing Al-O-Al bonds were active not only in benzene or n-heptane but also in some olefin solvents and the rate of polymerization in these solvents were found to be exceptionally high. It was also found that the formation of aloxanes plays an important role in the activation by  $H_2O$  of the cobalt catalyzed polymerization of butadiene [23].

Jang et al. investigated the activation of a metal alkyl free nickel based catalyst with  $B(C_6F_5)_3$  in the polymerization of butadiene and it was found to have high catalytic activity and 1, 4-cis stereoregularity. Variations in the molar ratio of  $B(C_6F_5)_3$  to nickel affected catalytic activity 1,4-cis stereoregularity and the Mw of polybutadiene and the rate of polymerization were found to be 1st order with respect to monomer concentration [24].

Throckmorton reported that the polymerization results obtained when the triethyl aluminum was replaced with other alkyl aluminium and  $BF_3Et_2O$  with other  $BF_3$  complexes or  $HF.Et_2O$  both the polymerization rate and the polymer viscosity decreased significantly as the length of the alkyl group in the alkyl aluminium increased from  $C_1$  to  $C_6$  [25].

Quirk et al. showed that higher and lower amounts of water, decreased conversion, broadened the molecular weight distribution and increased the molecular weight in BD polymerization using neodymium versate based catalyst [26].

BR-Nd have superior mechanical properties and the dynamic properties such as abrasion resistance, resistance to bending, fatigue, resilience and heat buildup. It is the potentially the best high-cis BR for applications that require high performance [1].

The polymerization of BD by neodymium versate, diisobutylaluminium hydride and tert-butyl chloride was studied by mello et al. and it was found that the cyclohexane

has marked effect on the polybutadiene molecular weight properties. The increasing cyclohexane content decreases the molecular weight and increases the molecular weight distribution [27].

The ternary catalyst system Nd (carboxylate)<sub>3</sub>/tertbutyl/diisobutyl aluminium hydride for the polymerization of 1,3-BD was studied with respect to halide/Nd ratio and halide type. And it was found that the lowering of the halide/Nd ratio result in lower conversion to polymer and a change in polymer molecular weight distribution [28].

Leo et al. presented a general scheme to explain in a qualitative and quantitative manner various features of Ziegler-type polymerization such as (1) the dependence of polymerization rate on monomer concentration,(2) the dependence of rate on aluminium alkyl ,(3) dependence of rate on catalyst ratio,(4) the factors upon which molecular weight depended (5) the effect of temperature on molecular weight,(6) the effect of temperature on polymerization rate, (7) the stereospecific polymerization aspects [29].

## 2.3 Scope and Objectives

In PBR-II plant of RIL-VMD, polybutadiene rubber is manufactured using nickel based catalyst system. This catalyst can be used in environment friendly solvents. From the above literature search it is observed that the detailed kinetics of nickel based system is not available in the open literature. Moreover, the detailed kinetic data of the reaction were not provided by the licensor of PBR-II plant. Hence, it is worth studying the kinetics of nickel based catalyst which will enrich the open literature as well as provide useful data to plant.

From the above literature survey, it is also observed that the cobalt-based catalysts were the most extensively studied in aromatic solvents. Many studies have been reported in the literature on kinetics of polymerization of 1, 3 butadiene using cobalt based catalyst. But most of the studies have been done in aromatic solvent, ben-

zene which is a known carcinogenic. PBR-I plant of RIL-VMD also uses benzene as solvent. Most of the cobalt based plants all over the world are shifting/ shifted to other environment friendly solvent routes. RIL-VMD is also committed to look for an alternative of benzene. Therefore, there is a scope to study the 1, 3-butadiene polymerization kinetics in non-carcinogenic solvent so that plant could be benefited while changing over the existing solvent to non-carcinogenic one.

**Objective:** To study the kinetics for polymerization of 1, 3 butadiene using nickel as well as cobalt based catalyst systems in environment friendly solvents.

**Parameters studied:**

a. (1) Parameters studied:

- Effect of  $BF_3.OEt_2/Et_3Al$  molar ratio on conversion.
- Effect of Nickel Naphthenate concentration on conversion.
- Effect of  $Et_3Al$  / Nickel Naphthenate concentration on conversion.
- Effect of  $Et_3Al$  concentration on conversion.
- Effect of polymerization time on conversion.

(2) Kinetic studies

- i. Polymerization time vs. conversion data at different monomer concentration.
- ii. Determination of order of reaction, rate constant, rate of reaction.
- iii. Determination of activation energy.

b. Cobalt based catalyst system

(1) Kinetic studies

- Polymerization time vs. conversion data at different monomer concentration.
- Determination of order of reaction, rate constant, rate of reaction.
- Determination of activation energy

# Chapter 3

## Experimental

### 3.1 Materials

#### 3.1.1 Monomer

1, 3- butadiene was obtained in 1 liter S.S. Bomb from PBR- II plant, RIL- VMD, Vadodara. It was purified by passing through two successive columns containing molecular sieves (3°) and triethyl aluminum solution respectively to remove moisture or any other impurities present before feed preparation.

#### 3.1.2 Solvents

Heptane-toluene mixed solvent (dry solvent 50:50) was obtained from PBR-II plant, RIL-VMD, Vadodara. Cyclohexane was obtained from Labort Fine Chem Pvt. Ltd., Surat.

#### 3.1.3 Catalysts

Nickel naphthenate (NIC), Triethyl aluminum (TEAL), Boron triflouride etherate (BRF) were obtained from PBR-II plant, RIL-VMD, Vadodara.. Cobalt Octanoate, Diethylaluminum chloride were obtained from PBR-I plant ,RIL-VMD, Vadodara.

### 3.1.4 Carbon Disulfide ( $CS_2$ )

Carbon Disulfide (GC 99.5% pure min) used as solvent for determination of Microstructure using FTIR 8000 series.  $CS_2$  was obtained from Labort Fine Chem Pvt. Ltd., Surat.

### 3.1.5 Short-stop

Methanol was obtained from PBR- I plant, RIL-VMD, Vadodara. Phosphate of polyoxyethylene alkyl phenyl ether (PPA) was obtained from PBR-II plant, RIL-VMD, Vadodara.

### 3.1.6 Antioxidant: Di-tertiary butyl p-cresol (DTBPC)

DTBPC was obtained from PBR-II plant, RIL-VMD, Vadodara. DTBPC was used as an antioxidant in methanol. 0.5% (w/v) of DTBPC solution in methanol was used to terminate the reaction.

## 3.2 Preparation of Feed

Schematic of feed preparation is shown in Scheme 3.1. 1, 3- butadiene was bubbled through traps containing 8% solution of triethylaluminum (TEAL) in toluene, activated molecular sieves ( $3A^\circ$ ), anhydrous KOH/ NaOH pellets and then into flask containing dry solvent at low temperature [keeping in ice or ice-salt mixture]. The concentration of dissolved 1, 3- butadiene at room temperature was estimated gravimetrically. The concentration was determined from the weight gain of the pre-weighed solvent in flask.

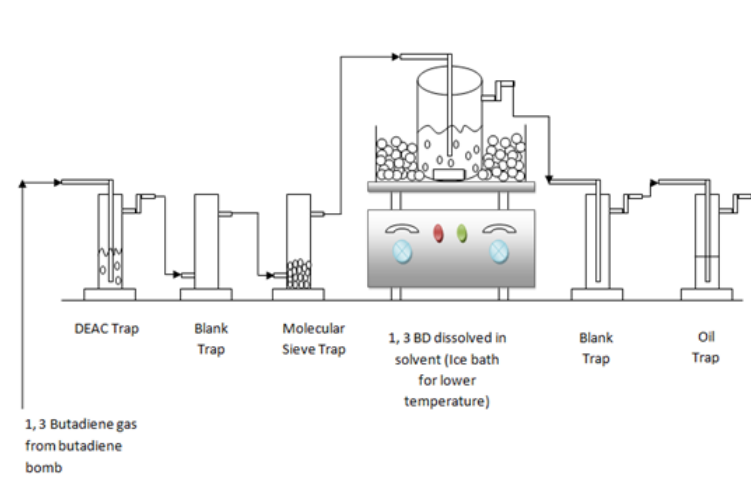


Figure 3.1: Feed preparation assembly

### 3.3 Polymerization

Polymerization reactor assembly is shown in Scheme 3.2

#### 3.3.1 Nickel based catalyst system

First all the catalysts (BRF/TEAL/NIC) were aged for 1 hour at  $20^{\circ}\text{C}$ . The temperature was maintained in the reactor with the help of temperature bath. Then the earlier prepared feed containing 20%BD in dry solvent was added to the reactor and the temperature was increased to  $60^{\circ}\text{C}$ . The reaction was conducted for 3h. Then the calculated amount of PPA was added to the reactor to kill the catalyst activity.

#### 3.3.2 Cobalt Based catalyst system

First of all the earlier prepared feed containing 20-22%BD in cyclohexane was added to the reactor at  $20^{\circ}\text{C}$ . Then extra water, DEAC, cobalt octanoate, 1,5-COD was added to the reactor. The reaction was conducted for 1h. Then the Methanol was added to the reactor to kill the catalyst activity. 1. Nitrogen line; 2. Port for charging raw materials; 3. Thermocouple; 4. Magnetic motor; 5. Bottom outlet.



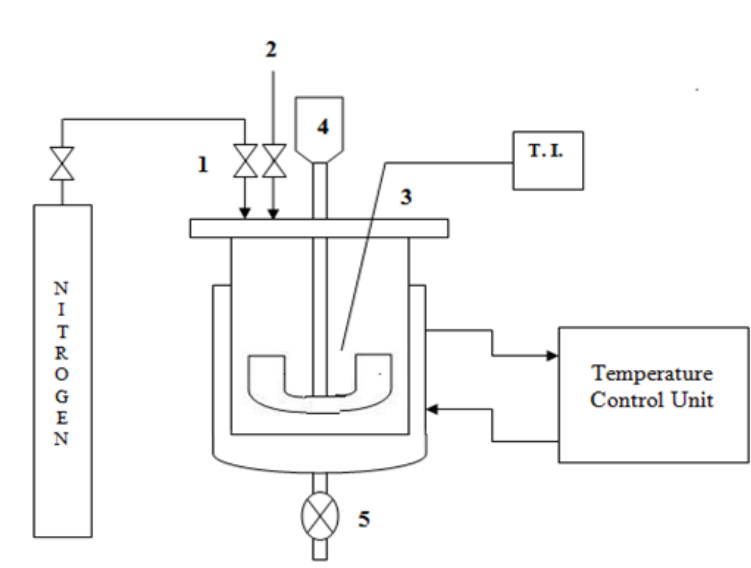


Figure 3.2: 1, 3 Butadiene Polymerization Assembly (Buchi Diagram)

### 3.4 Polymer Recovery

As the reaction proceeds, the reaction mass becomes viscous and this is the indication of polymer formation. Polymerization was terminated with PPA and coagulated with methanol containing 0.5% of di-tert-butyl-para-cresol. Rubber comes out of solution when methanol is added. Then the rubber was separated by decantation.

### 3.5 Sample Drying

The sample was kept on a glass Petri dish in fuming hood at room temperature for one day. Then it was cut in small pieces. Sample was placed in a vacuum oven at  $45^{\circ}\text{C}$  for 6h under vacuum.

### 3.6 Sample Drying

The sample was kept on a glass Petri dish in fuming hood at room temperature for one day. Then it was cut in small pieces. Sample was placed in a vacuum oven at  $45^{\circ}\text{C}$  for 6h under vacuum.

### 3.7 Conversion

Conversion was calculated taking the ratio of output to input where output is 1, 4-butadiene rubber and input is 1, 3 butadiene monomer. % Conversion = (rubber produced / monomer fed) \* 100

### 3.8 Microstructure

Cis, vinyl and trans-contents are determined by PERKIN ELMER 1600 Series FTIR spectrophotometer using frequencies at 740, 912 and  $965\text{cm}^{-1}$  respectively. Sample was prepared by taking 75mg of rubber in 10ml of  $CS_2$

### 3.9 Gel-permeation chromatography

Molecular weight and molecular weight distribution were studied using gel-permeation chromatography (Perkin Elmer, USA).

### 3.10 Safety precautions

All the chemicals were handled under the fume hood with all the protection protective equipments that is safety glasses, lab coat, mask, hand gloves etc.

# Chapter 4

## Results And Discussion

In the present thesis the polymerization of butadiene with nickel based catalyst system is examined in details. Nickel based catalyst system is comprised of Nickel Naphthenate (NIC), Boron Trifluoride (BRF), Triethylaluminium (TEAL). The mechanism of butadiene polymerization with this catalyst system is shown in Scheme 4a. In presence of BRF, TEAL acts as alkylating agent. TEAL alkylates the nickel naphthenate (NIC) and changes its coordination geometry from Oh to Td and generates a vacant site where monomer can attach and thus facilitating the polymerization (Scheme 4a). In absence of BRF, TEAL reduces the NIC to Ni (0) and polymerization cannot take place. Thus, BRF/TEAL ratio plays a vital role in this polymerization. In the established technology, these catalyst components are aged before transferring to the polymerization reactor. The effect of catalyst ageing was then studied first. Where, R1-COO = naphthenate, R2 =Et, x+y=3

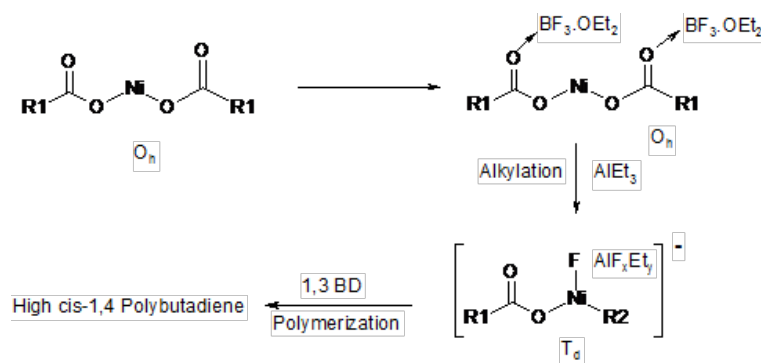


Figure 4.1: Mechanism of polymerization

## 4.1 Effect of catalyst ageing on polymerization of 1, 3-butadiene

Catalyst ageing plays a major role on polymerization. Polymerization is more vigorous without ageing. The rubber produced without ageing and after ageing of catalysts is compared in Table I. Ageing temperature is again a critical parameter. The plot

Table I: Effect of catalyst ageing on characteristics of rubber

Characteristics	Without ageing	With ageing
Conversion at 2h, %	88	52
Microstructure		
Cis, %	97.35	97.22
Trans, %	1.89	0.81
Vinyl, %	0.74	1.96
Density, gcm <sup>-3</sup>	0.92	0.88
Mooney viscosity, ML1+4@100°C	41	48
Weight average molecular weight, lacs	2.86	3.21
Polydispersity index	3.41	2.86

of conversion vs. ageing temperature at constant ageing time is shown in Fig 4.2.

The conversion is maximum at the ageing temperature of 20°C. Above or below this particular temperature conversion is lower. This may be due to thermal degradation of active sites at higher temperature. At lower temperature, number of the active site formed is lower at a constant time compared to 20°C. Hence, afterwards, catalysts were aged at 20°C.

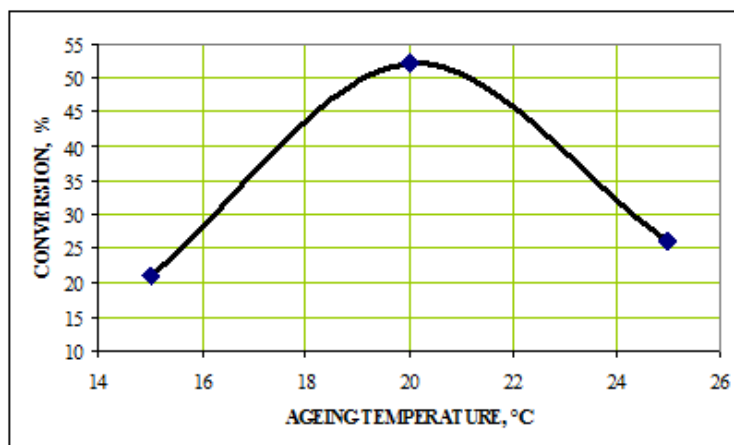


Figure 4.2: Effect of ageing temperature on conversion

**Polymerization Conditions:** Monomer = 2.64mol/l, Catalyst ageing time = 60min, Reaction temperature = 60°C, Reaction time =180min, NIC = 3.8mmphgm\*, TEAL =39mmphgm, BRF/TEAL=1.07;

\*mmphgm = millimole per hundred gram of monomer.

## 4.2 Effect of BRF/TEAL ratio on polymerization of 1, 3-butadiene

Table II indicates the catalyst dosing at which the runs were made to determine the effects of BRF/TEAL molar ratio on conversion. Fig-4.3 shows the dependence of BRF/TEAL ratio on conversion. This plot indicates that the conversion increases upto 56% at a certain BRF/TEAL ratio (1.07) and then it again decreases. This observation is in accordance with existing literatures [14]. Hence, BRF/TEAL ratio

is optimized at 1.07 and further reactions are taken with this ratio. With increasing co-catalyst [TEAL] concentration, conversion initially increases exponentially upto 56% at 39mmphgm after which it again decreases.

Table II: Effect of BRF/TEAL ratio on conversion

Triethylaluminum (TEAL) (mmphgm*)	Boron Tri-fluoride Etherate (BRF) (mmphgm*)	Nickel Naphthen-ate (NIC) (mmphgm*)	BRF/TEAL [molar ratio]	Conversion (%)
64	42.11	3.8	0.65	25
39	42.11	3.8	1.07	56
33	42.11	3.8	1.27	28
26	42.11	3.8	1.60	0

\*mmphgm = millimole per hundred gram of monomer

**Polymerization Conditions:** Monomer concentration= 3.22mol/l, Catalyst ageing temperature = 20°C, Catalyst ageing time = 60min, Reaction temperature = 60°C, Reaction time =120min

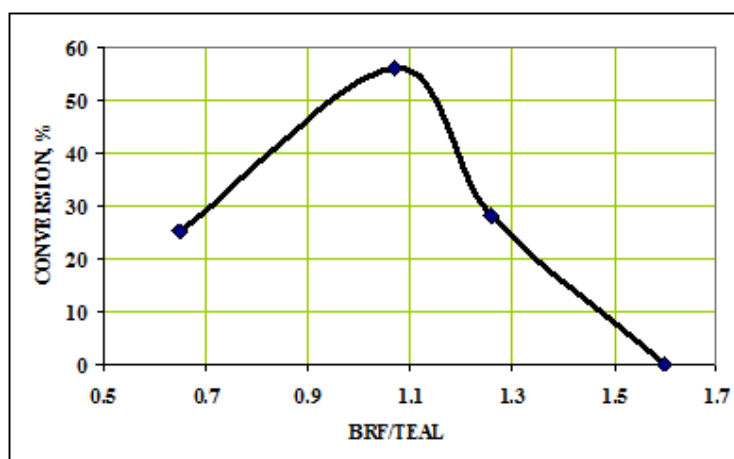


Figure 4.3: Plot of BRF/TEAL vs. conversion

### 4.3 Effect of catalyst (NIC) concentration on polymerization of 1, 3-butadiene

Table III reports the catalyst dosing at which the runs were made to determine the effect of NIC on conversion. The curve in the Fig 4.4 shows that the conversion increases with the increase in concentration of NIC upto certain concentration (3.8 mmphgm) after which it decreases with increase in the concentration of NIC.

Table III: Effect of catalyst (NIC) concentration on conversion

Triethylaluminum (TEAL) (mmphgm)	Boron Trifluoride Etherate (BRF) (mmphgm)	Nickel Naphthenate (NIC) (mmphgm)	Conversion (%)
18	19.26	1.8	1
28	30.00	2.8	14
39	42.11	3.8	56
48	51.36	4.8	25

**Polymerization Conditions:** Monomer = 3.22mol/l, Catalyst ageing temperature = 20°C, Catalyst ageing time = 60min, Reaction temperature = 60°C, Reaction time =120min, BRF/TEAL=1.07

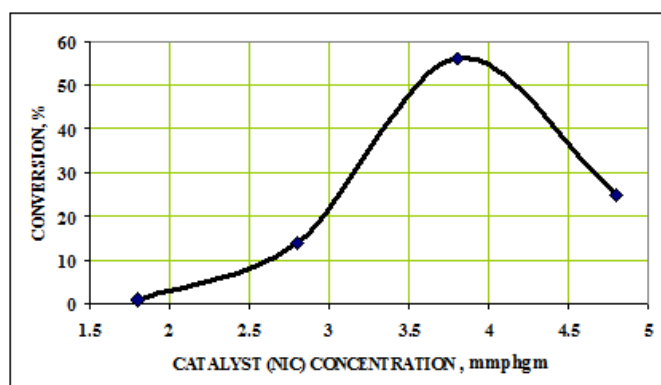


Figure 4.4: Plot of catalyst concentration vs. conversion

## 4.4 Effect of catalyst (NIC) concentration on polymerization of 1, 3-butadiene

Fig4.5 illustrates the effect of monomer concentration on polymerization of 1, 3-butadiene. Conversion goes through maxima with increasing monomer concentration. Maximum conversion was obtained at 2.32 mol/l of monomer.

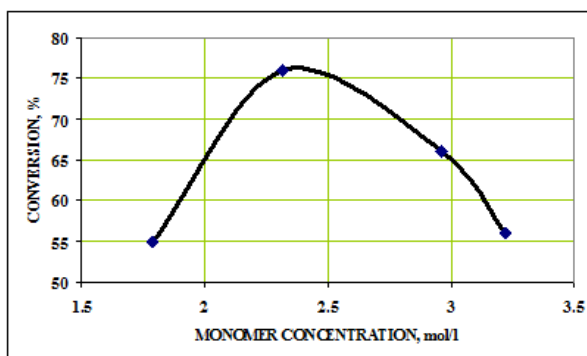


Figure 4.5: Plot of monomer concentration vs. conversion

**Polymerization Conditions:** Catalyst ageing temperature = 20°C, Catalyst ageing time = 60min, Reaction temperature = 60°C, Reaction time = 120min., NIC=3.8mmphgm, TEAL = 39mmphgm, BRF/TEAL = 1.07

## 4.5 Characterization of the polymers

### Molecular weight and molecular weight distribution:

Plot of weight average molecular weight ( $M_w$ ) of polymers with conversion is shown in Fig-4.6.  $M_w$  increases linearly with increasing conversion indicating living nature of the polymerization. It indicates that appreciable chain termination did not take place at the given polymerization condition. There is a sudden drop in polydispersity index (PDI) with increasing conversion, thereafter it almost remains constant.



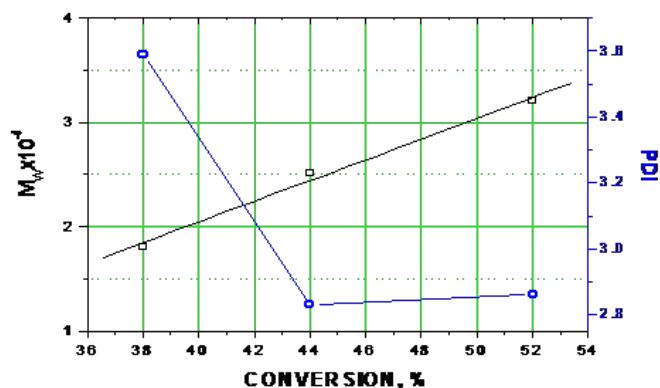


Figure 4.6: Effect of conversion on Mw and PDI of the polymer

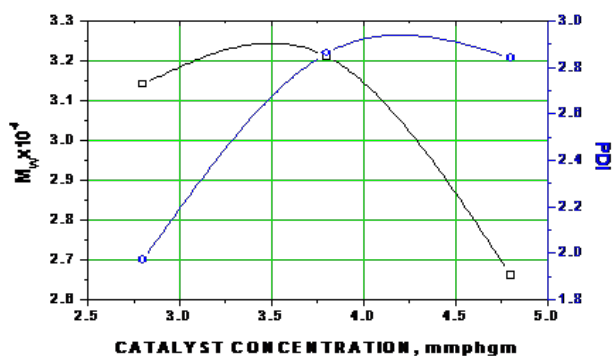


Figure 4.7: Effect of catalyst concentration on Mw and PDI

Effect of catalyst concentration on the characteristics of the polymer is shown in Fig 4.7. At lower catalyst concentration Mw is higher and decreases at higher catalyst dose. The PDI shows a reverse trend. At lower catalyst concentration, lower number of active sites, provokes a molecular weight increase.

Fig-4.8 shows the effect of temperature on Mw and PDI of polymer. Mw increases whereas PDI decreases with increasing temperature. The Mw of different samples ranges from 2.7 to 3.9 lacs, whereas PDI is in the range of 2.0 to 3.6. The PBR-II plant samples show the Mw values in the range of 3.0 – 4.0 lacs and PDI values in the range of 2.7-3.0.

#### Microstructure:

The microstructure of different polymers synthesized using various catalyst concen-

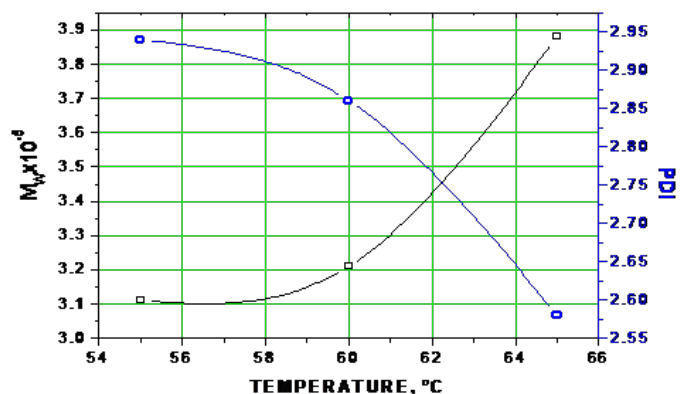


Figure 4.8: Effect of temperature on Mw and PDI

trations are reported in Table IV. All the samples show a *cis*-content of >97%, around 2% of *trans*-content and rest *vinyl*-content. Neither catalyst concentration nor temperature has any pronounced effect on microstructure. PBR-II plant samples also show *cis*-content of >97%.

Table IV: Microstructure of different polymers

Catalyst concentration, (mmphgm)	Temperature, °C	Microstructure		
		Cis, %	Vinyl, %	Trans, %
2.8	60	97.62	0.70	1.68
3.8	60	97.22	0.81	1.96
4.8	60	97.43	0.72	1.84
3.8	55	97.74	0.69	1.56
3.8	65	97.37	0.75	1.89

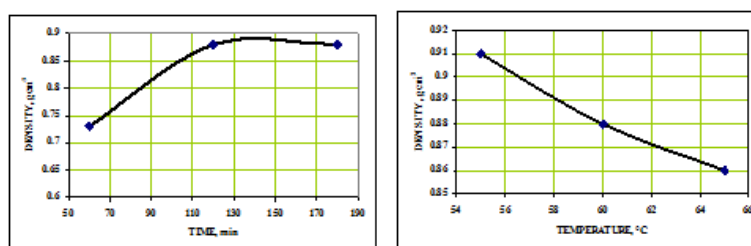


Figure 4.9: Effect of polymerization [a] time and [b] temperature on density of the elastomer

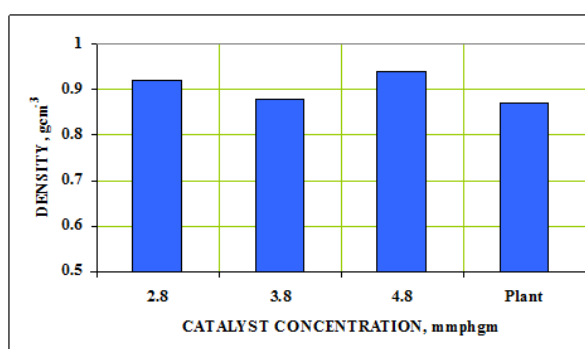


Figure 4.10: Effect of catalyst concentration on density of the elastomer

### Density:

Fig 4.9 and 4.10 shows the effect of different polymerization parameters on density of the synthesized elastomer. Density increases with polymerization time and reaches a plateau whereas it decreases gradually with increasing temperature. Fig 4.10 illustrates the effect of catalyst concentration on the density of the elastomer. Density varies in the range of  $0.86\text{-}0.94\text{gcm}^{-3}$ . Density of elastomer synthesized at  $60^{\circ}\text{C}$  using  $3.8\text{mmphgm}$  of catalyst is similar to that of the plant sample.

**Mooney viscosity:**

Mooney viscosity of the elastomer, synthesized at optimum condition, is 48 (ML1+4@100°C), which is in the range of prime grade product. Prime grade product of plant has a Mooney viscosity range of 38-50 (ML1+4@100°C).

## 4.6 Kinetic Studies

The recipe for the kinetic studies was decided as per the above optimized doses. Monomer: 2.32mol/l NIC = 3.8mmphgm TEAL = 39mmphgm BRF/TEAL= 1.07 Catalyst ageing temperature was 20°C, catalyst ageing time was 60min, and reaction temperature was 60°C [unless otherwise mentioned].

A typical plot of time vs. conversion is shown in Fig 4.11. Initially polymerization proceeds rapidly after that it slows down. The curve does not pass through the origin due to slight formation of polymer during the heating period prior to the normal polymerization.

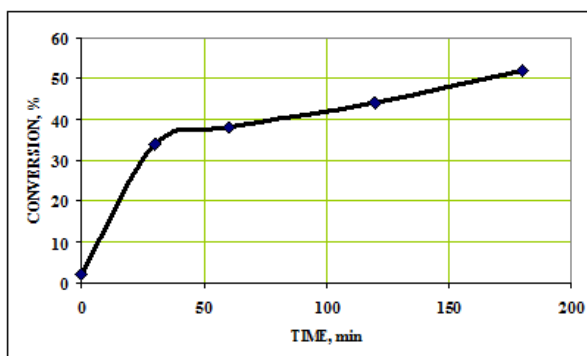


Figure 4.11: Course of the conversion as a function of time

The following equation is considered for the kinetics of the stereo specific polymerization of butadiene in solution [18]:

$$\frac{-dC_M}{dt} = k [C_M]^a [C_C]^b \quad (4.1)$$

Where,  $\frac{-dC_M}{dt}$  = Rate of disappearance of monomer or rate of polymerization.

$k$  = Rate constant

$C_M$  = Monomer concentration, moles/l

$a$  = Reaction order with respect to monomer concentration.

$C_C$  = Catalyst concentration.

$b$  = Reaction order with respect to catalyst concentration

$t$  = Reaction time

The order of the reaction with respect to monomer and to catalyst was determined and the value of overall rate constant,  $k$ , and the activation energy were calculated.

Considering the catalyst concentration as constant, equation [4.1] becomes

$$\frac{-dC_M}{dt} = k_1 [C_M]^a \quad (4.2)$$

#### **Determination of reaction order with respect to monomer**

Time-conversion relations were found to be described best by the 1<sup>st</sup> order equation with respect to the monomer concentration. The check with the 1st order relation was made as follows. The first order differential equation [4.2], is integrated between  $C_{M0}$  to  $C_M$  and  $t$  to  $t_0$ .

$$-\ln \left( \frac{C_M}{C_{M0}} \right) = k_1 (t - t_0) \quad (4.3)$$

$$-\ln (1 - x) = k_1 (t - t_0) \quad (4.4)$$

$$-\ln (1 - x) = k_1 t \quad (4.5)$$

Where, the constant  $t_0$  appears in the equation [4] as an integral constant and is equal to the time elapsed before the first order reaction started. It may be called induction period. and the initial concentration of the monomer is denoted by  $C_{M0}$

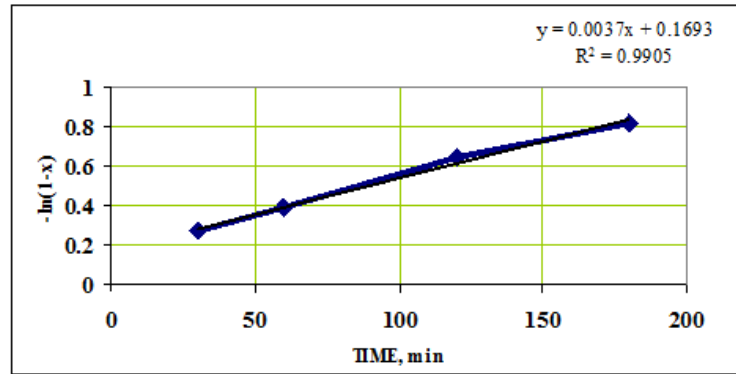
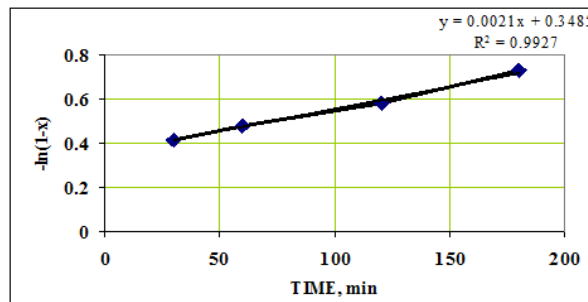
and  $x$ , fractional conversion, is given by the following equation:

$$x = 1 - \frac{C_M}{C_{M0}} \quad (4.6)$$

The experimental time-conversion data were checked with the equation Eq. [4] for different monomer concentrations (Table-V) as shown in Fig 4.12,13 and 14.

Table V: Polymer conversion at various monomer concentrations at constant catalyst concentration and temperature

Time (min)	Weight of rubber obtained (g)	Conversion (%)	Initial Monomer, $C_{M0}$ (mol/l)	Final Monomer, $C_M$ (mol/l)	Fractional Conversion, $x = 1 - \frac{C_M}{C_{M0}}$	$-\ln(1-x)$
30	8	24	1.800	1.376	0.235	0.268
60	11	32	1.800	1.217	0.324	0.391
120	16	48	1.800	0.939	0.478	0.650
180	19	56	1.800	0.794	0.559	0.818
30	15	30	2.640	1.852	0.299	0.355
60	19	38	2.640	1.640	0.379	0.476
120	20	40	2.640	1.587	0.399	0.509
180	26	52	2.640	1.276	0.517	0.727
30	12	21	2.960	2.328	0.214	0.241
60	14	25	2.960	2.222	0.250	0.288
120	15	27	2.960	2.169	0.268	0.312
180	20	36	2.960	1.905	0.357	0.442

Figure 4.12: 1<sup>st</sup> order plot of the polymerization [at monomer concentration 1.8mol/l]Figure 4.13: 1<sup>st</sup> order plot of the polymerization [at monomer concentration 2.64mol/l]

Linear relations can be found except in early stages of the polymerization. Most of the monomer is consumed in the stage where the rate of reaction depends upon the first order of the concentration of the remaining monomer. In this sense of approximation, it may be concluded that first order relation is applicable during the polymerization except for the initial short period. These plots indicate, from the linearity of the curves, after that induction period that the reaction is truly of 1st order with respect to the monomer. Now, we can put  $a = 1$  in equation (4.1) to have

$$\frac{-dC_M}{dt} = k [C_M] [C_C]^b \quad (4.7)$$

Integrating equation[4.7]

$$\frac{-\ln\left(\frac{C_M}{C_{M0}}\right)}{t} = k [C_C]^b \quad (4.8)$$

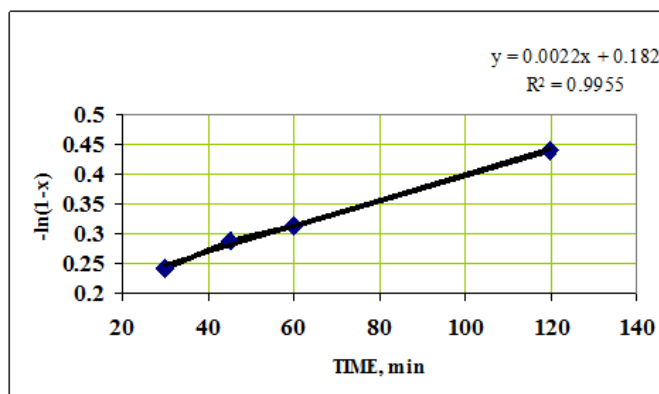


Figure 4.14: 1<sup>st</sup> order plot of the polymerization [at monomer concentration 2.96mol/l]

Plot of  $-\ln(1-x)$  vs.  $t$  (Fig 4.15) at constant monomer concentration but at different catalyst concentrations shows a dependence of reaction rate on the monomer concentration.

The slope of the lines in Fig 4.15 gives the rate constant at each catalyst concentration.

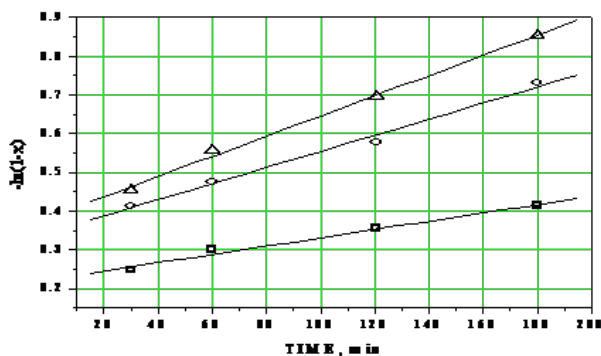


Figure 4.15: 1st order plot of the polymerization of butadiene, at monomer concentration= 2.64mol/l, and at catalyst concentration of  $\circ$  2.8 mmphgm,  $\Delta$  3.8 mmphgm and  $\square$  4.8 mmphgm

These rate constant values are plotted as a function of the catalyst concentration [keeping the molar ratio of catalyst-co-catalyst and promoter constant] (Fig. 4.16). Since, the points fall on a straight line, we can conclude that  $b$  must be equal to 1, i.e., the polymerization rate with respect to the catalyst concentration is of the 1<sup>st</sup>



order. The slope of the line in Fig. 4.10 is as follows

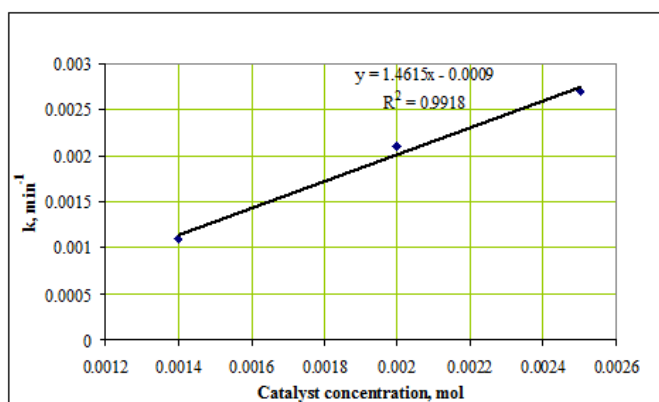


Figure 4.16: Plot of  $k$  as a function of catalyst concentration

#### Determination of activation energy:

The activation energy is determined according to the Arrhenius equation:

$$k = f(T) = Ae^{-E/RT}$$

Where  $T$  is absolute temperature.

For this purpose, polymerization reactions were taken at 55, 60 and 65°C at constant concentration of catalyst and monomer.

In Fig. 4.17,  $-\ln(1-x)$  as a function of time at various temperatures is plotted.

Rate constants at different temperatures are calculated from the slope of the lines plotted in Fig 4.17. The values of rate constants are reported in Table VI.

Log  $k$  vs.  $1/T$  is plotted in Fig. 4.18.

The slope of the line =  $\frac{-E}{2.3R} = -3183.7$   $R = 1.98 \text{ cal K}^{-1} \text{ mol}^{-1}$

So, activation energy,  $E = 14499 \text{ cal mol}^{-1} = 14.5 \text{ kcal mol}^{-1}$

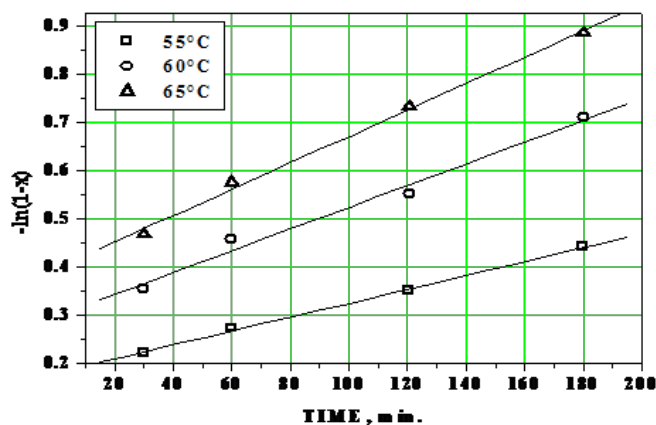


Figure 4.17: Effect of temperature on reaction rate

Table VI: Effect of temperature on reaction rate

Temperature, °C,	$k$ , min <sup>-1</sup>	1/T	log $k$
55	0.0014	0.00305	- 2.8539
60	0.0021	0.00300	- 2.6778
65	0.0027	0.00296	- 2.5686

## Part 2: Polymerization of 1, 3 butadiene using cobalt catalyst

The literature studies showed that cobalt catalyst system works excellent in aromatic solvents. But due to environmental hazards, solvent system has been gradually shifting to non-carcinogenic solvents. In RIL-VMD, detail studies on the effect of catalyst dosing, monomer concentration and temperature have already been done [30] But detailed kinetic studies is not available. So, in this part of the dissertation, butadiene polymerization and its kinetics were studied in the non-carcinogenic solvent, cyclohexane The mechanism of cobalt catalyzed butadiene polymerization is shown in figure 4.19

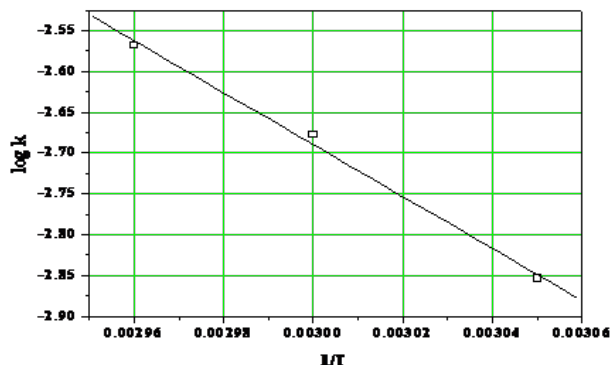


Figure 4.18: Plot of log k vs. 1/T

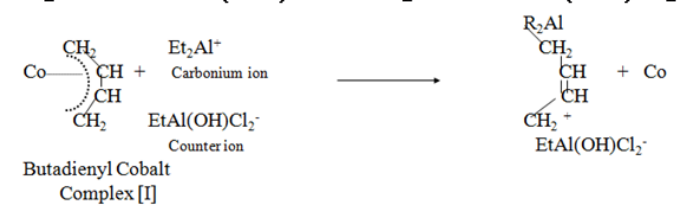
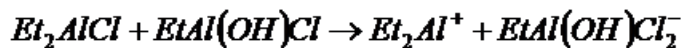
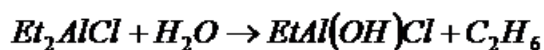


Figure 4.19: Mechanism of in-situ generation of different Lewis acidity from the reaction of DEAC and water and its effect on polymerization

## 4.7 Kinetics studies

The recipe for the kinetic studies was decided as per the optimized doses.[30]

Monomer: 2.59mol/l Cobalt Octanoate = 0.02mmphgm Diethylaluminium chloride = 5mmphgm W/A=0.22 Reaction time was 60min, and reaction temperature was 20°C [unless otherwise mentioned.]

A typical plot of time vs. conversion is shown in Fig. 4.20. Initially polymerization proceeds rapidly after that it becomes almost constant. This observation is according to the published literature.[31] The following equation is considered for the kinetics of the stereo specific polymerization of butadiene in solution [18]:

$$\frac{-dC_M}{dt} = k [C_M]^a [C_C]^b \quad (4.9)$$

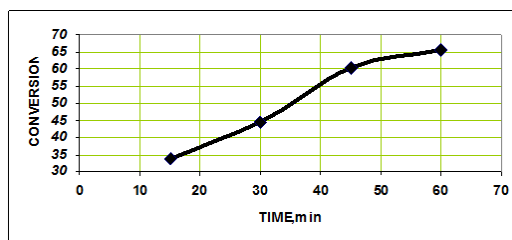


Figure 4.20: Course of the conversion as a function of time

Where,  $\frac{-dC_M}{dt}$  = Rate of disappearance of monomer or rate of polymerization.

$k$  = Rate constant  $C_M$  = Monomer concentration, moles/l  $a$  = Reaction order with respect to monomer concentration.  $C_C$  = Catalyst concentration.  $b$  = Reaction order with respect to catalyst concentration  $t$  = Reaction time The order of the reaction with respect to monomer and to catalyst was determined and the value of overall rate constant,  $k$ , and the activation energy were calculated.

Considering the catalyst concentration as constant, equation (4.1) becomes:

$$\frac{-dC_M}{dt} = k_1 [C_M]^a \quad (4.10)$$

#### Determination of reaction order with respect to monomer:

Time-conversion relations were found to be described best by the 1<sup>st</sup> order equation with respect to the monomer concentration. The check with the 1<sup>st</sup> order relation was made as follows. The first order differential equation (4.2), is integrated between  $C_{M0}$  to  $C_M$  and  $t$  to  $t_0$ .

$$-\ln \left( \frac{C_M}{C_{M0}} \right) = k_1 (t - t_0) \quad (4.11)$$

$$-\ln (1 - x) = k_1 (t - t_0) \quad (4.12)$$

$$-\ln (1 - x) = k_1 t \quad (4.13)$$

Where,  $t_0 = 0$  appears in the equation (4.4) as an integral constant and is equal to the time elapsed before the first order reaction started .It may be called induction

period and the initial concentration of the monomer is denoted by  $C_{M0}$  and  $x$ , fractional conversion, is given by the following equation:

$$x = 1 - \frac{C_M}{C_{M0}} \quad (4.14)$$

The experimental time-conversion data for different monomer concentrations (Table VII) were fitted with equation (4.4) and shown in Fig. 4.21-23.

Table VII: Polymer conversion at various monomer concentrations at constant catalyst concentration and temperature

Time (min)	Weight of rubber obtained (g)	Conversion (%)	Initial Monomer, $C_{M0}$ (mol/l)	Final Monomer, $C_M$ (mol/l)	Fractional Conversion, $x = 1 - \frac{C_M}{C_{M0}}$	$-\ln(1-x)$
15	0.0070	12	0.0011	0.0009	0.1182	0.1258
30	0.0018	13	0.0026	0.0023	0.1278	0.1367
45	0.0020	15	0.0025	0.0024	0.1451	0.1568
60	0.0024	16	0.0026	0.0022	0.1699	0.1862
5	0.0019	24	0.0015	0.0011	0.2417	0.2767
15	0.0027	25	0.0019	0.0014	0.2566	0.2965
30	0.0037	29	0.0022	0.0016	0.2983	0.3543
45	0.0076	31	0.0044	0.0030	0.3135	0.3761
15	0.0046	33	0.0025	0.0016	0.3377	0.4120
30	0.0428	44	0.0178	0.0099	0.4434	0.5859
45	0.0047	60	0.0014	0.0005	0.6025	0.9227
60	0.0050	66	0.0015	0.0004	0.6544	1.0626

These plots indicate, from the linearity of the curves, that the reaction is truly of 1<sup>st</sup> order with respect to the monomer. Now, we can put  $a=1$  in equation (4.1) to have

$$\frac{-dC_M}{dt} = k [C_M] [C_C]^b \quad (4.15)$$

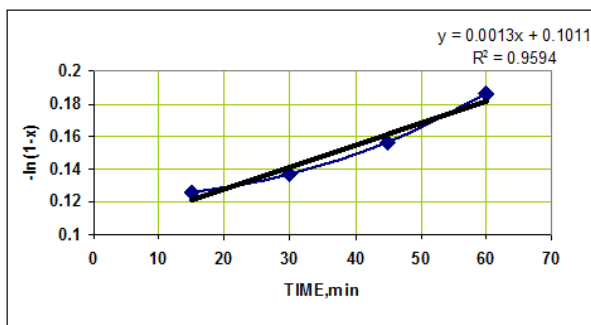


Figure 4.21: 1<sup>st</sup> order plot of the polymerization [at monomer concentration 1.29mol/l]

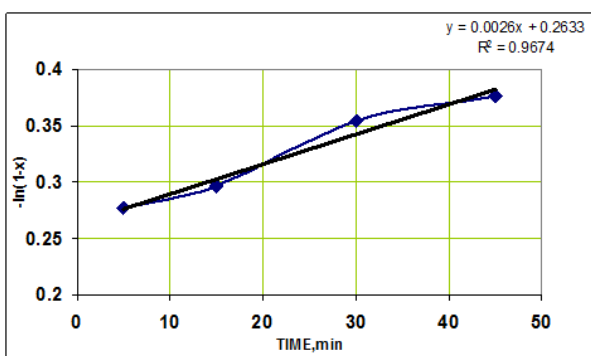


Figure 4.22: 1<sup>st</sup> order plot of the polymerization [at monomer concentration 1.85mol/l]

Integrating equation (4.7)

$$\frac{-\ln\left(\frac{C_M}{C_{M0}}\right)}{t} = k [C_C]^b \quad (4.16)$$

$$\frac{-\ln(1-x)}{t} = k [C_C]^b \quad (4.17)$$

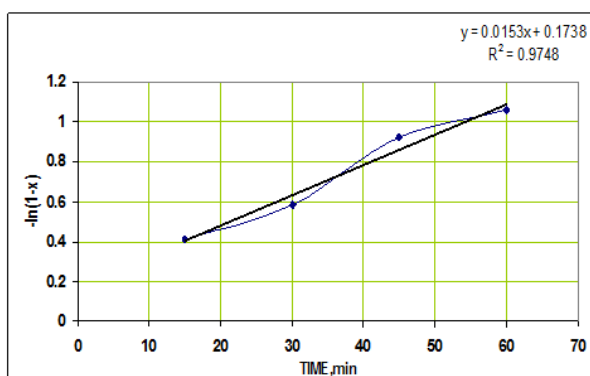


Figure 4.23: 1<sup>st</sup> order plot of the polymerization [at monomer concentration 2.59mol/l]

Plot of  $-\ln(1-x)$  vs.  $t$  (Fig. 4.24-26) at constant initial monomer concentration but at different catalyst concentrations shows a dependence of reaction rate on the catalyst concentration.

The slope of the lines in Fig. 4.24-26 gives the rate constant at each catalyst concentration.

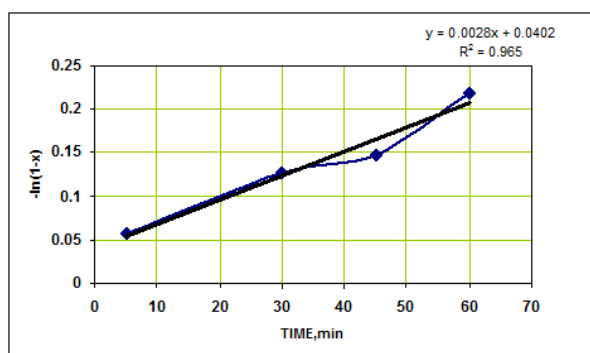


Figure 4.24: 1<sup>st</sup> order plot of the polymerization of butadiene, at monomer concentration= 2.59mol/l, and at catalyst concentration 0.01mmphgm

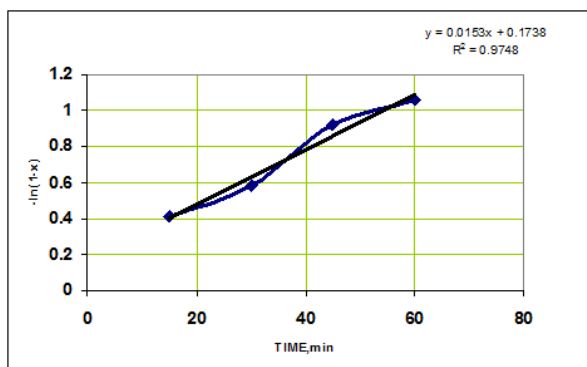


Figure 4.25: 1<sup>st</sup> order plot of the polymerization of butadiene, at monomer concentration= 2.59mol/l, and at catalyst concentration 0.02mmphgm

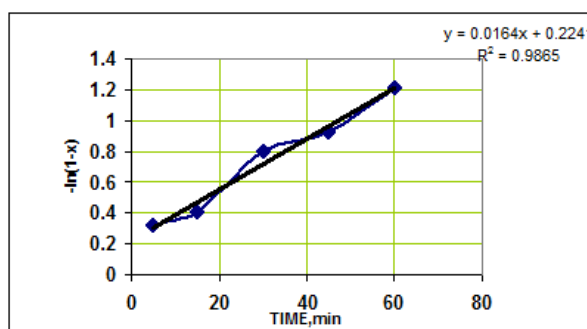


Figure 4.26: 1<sup>st</sup> order plot of the polymerization of butadiene, at monomer concentration= 2.59mol/l, and at catalyst concentration 0.03mmphgm

These rate constant values are plotted as a function of the catalyst concentration [keeping the molar ratio of catalyst-co-catalyst and promoter constant] [Fig. 4.27]. Since, the points fall on a straight line, we can conclude that  $b$  must be equal to 1, i.e., the polymerization rate with respect to the catalyst concentration is of the 1<sup>st</sup> order.

The slope of the line in Fig. 10 is as follows:  $\frac{-\ln(1-x)/t}{[C_C]} = k = 0.68 \text{ min}^{-1} \text{ mol}^{-1}$ , which is overall rate constant.

**Determination of activation energy:** The activation energy is determined according to the Arrhenius equation:

$$k = f(T) = Ae^{-E_a/RT} \quad (4.18)$$



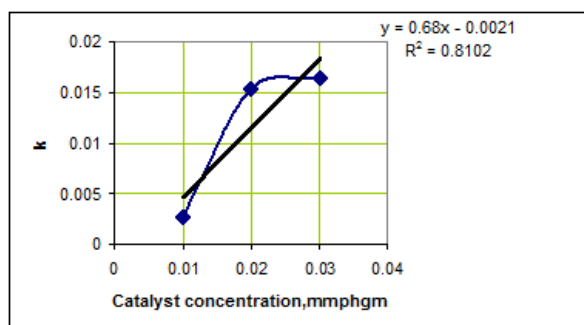


Figure 4.27: Plot of  $k$  as a function of catalyst concentration

Where  $T$  is absolute temperature.

For this purpose, polymerization reactions were taken at 10, 20 and 25°C at constant concentration of catalyst and monomer.

In Fig. 4.28-30,  $-\ln(1-x)$  as a function of time at various temperatures is plotted.

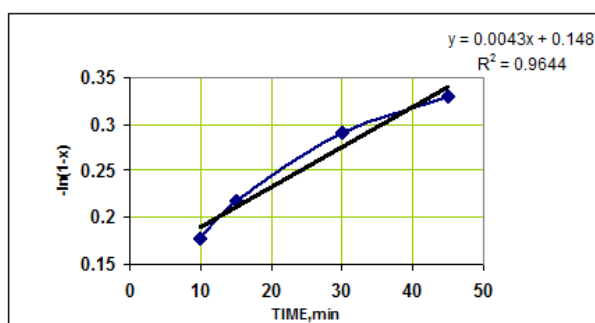


Figure 4.28: Effect of temperature on reaction rate at 10°C

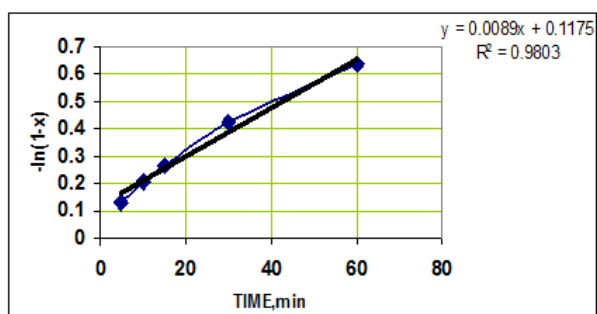


Figure 4.29: Effect of temperature on reaction rate at 20°C

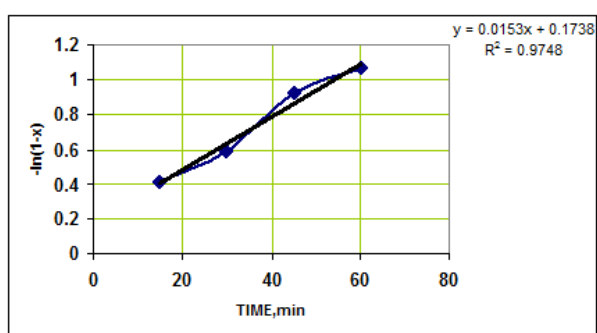


Figure 4.30: Effect of temperature on reaction rate at 25°C

Rate constants at different temperatures are calculated from the slope of the lines plotted in Fig.4.28-30. The values of rate constants are reported in Table VIII

Table VIII: Effect of temperature on reaction rate

Temperature, oC	$k$ , min <sup>-1</sup>	1/T	log $k$
10	0.0043	0.00353	-2.3665
20	0.0089	0.00341	-2.0506
25	0.0153	0.00335	-1.8153

Log  $k$  vs.  $1/T$  is plotted in Fig. 4.31. The slope of the line =  $\frac{-E}{2.3R} = -3025.1$

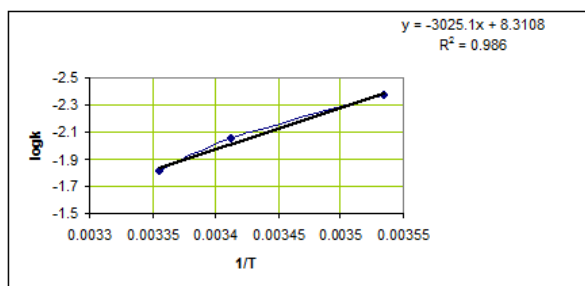


Figure 4.31: Plot of log  $k$  vs.  $1/T$

$$R = 1.98 \text{ cal K}^{-1} \text{ mol}^{-1}$$

So, activation energy,  $E = 13776 \text{ cal mol}^{-1} = 13.7 \text{ kcal mol}^{-1}$ .

# Chapter 5

## Conclusion

In PBR-II plant of RIL-VMD, polybutadiene is manufactured using nickel based catalyst system consisting of nickel naphthenate [catalyst], boron trifluoride etherate [promoter], triethylaluminium [co-catalyst]. The detailed kinetic data of the reaction were not provided by the licensor of PBR-II plant. Moreover, the kinetics of nickel based system is not readily available in the open literature. Hence, in this work, effect of nickel based Ziegler-Natta catalyst system on polymerization of 1, 3- butadiene and its detailed kinetics in an environment friendly solvent system (toluene: heptane 50:50) was studied.

Besides, PBR-I plant of RIL-VMD utilizes benzene as the solvent for the polymerization of 1, 3-butadiene using cobalt based catalyst system. The cobalt catalyst system comprises of cobalt octanoate [catalyst], diethylaluminium chloride [co-catalyst] and water [promoter]. Benzene is a carcinogenic solvent which leads to Hematoxin that is linked to increased incidence of leukaemia in humans. So, in this study an attempt was taken to study the 1, 3-butadiene polymerization kinetics in non-carcinogenic cyclohexane solvent so that plant could be benefited while changing over the existing solvent to non-carcinogenic one.

From this study, the following conclusions can be made.

- Catalyst ageing temperature plays a major role in the final conversion in case

of nickel based catalyst system.

- Ratio of promoter to co-catalyst is one of important parameters governing the polymerization in case of both the catalyst systems.
- Polymerization is 1st order with respect to monomer concentration as well as catalyst concentration in case of both the catalyst systems.
- The overall rate constant was found to be  $1.462 \text{ min}^{-1}\text{mol}^{-1}$  for nickel based catalyst system. The activation energy of the polymerization based on this catalyst system was found to be  $14.5\text{kcal mol}^{-1}$ .
- The overall rate constant was found to be  $0.68 \text{ min}^{-1}\text{mol}^{-1}$  for cobalt based catalyst system. The activation energy of the polymerization based on this catalyst system was found to be  $13.7\text{kcal mol}^{-1}$ .

# Chapter 6

## Scope for further work

Due to time constraint, some of factors could not be studied in the present thesis which can be taken up in future.

a. Nickel based catalyst system

- In this study, the effect of ageing temperature on polymerization of 1,3-butadiene was studied. Further, there is scope for studying the effect of ageing time on polymerization.
- There is scope for further studying the final product properties such as physico-mechanical, rheological and dynamic mechanical properties.
- In the present report, the overall kinetics was done for the polymerization of 1, 3-butadiene. Individual rate constants for each step of polymerization e.g., rate of initiation, propagation and termination can be found in the future.
- One could do the mathematical modelling for the kinetics of polymerization of 1, 3- butadiene.

## b. Cobalt based catalyst system

- In this study, only one non-carcinogenic solvent was studied. Other solvents or solvents mixture can be taken into consideration for further studies.
- There is scope for further studying the final product properties such as physico-mechanical, rheological and dynamic mechanical properties.
- In the present study, the overall kinetics was done for the polymerization of 1, 3-butadiene. Individual rate constants for each step of polymerization e.g. rate of initiation, propagation and termination can be found in the future.
- One could do the mathematical modelling for the kinetics of polymerization of 1, 3- butadiene based on this catalyst system.

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