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ORIGINAL PAPER

# Optimization of 1,3-butadiene monomer coordination polymerization using response surface methodology (RSM)

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## ABSTRACT

Laboratory runs can be minimized via experimental design which yields the optimum and best data regarding the independent parameters. In this research work, response surface methodology (RSM) based on a three-level central composite design (CCD) was utilized to optimize and evaluate the interactive effects of processing conditions for polymerization of 1,3-butadiene (Bd) diene monomer using Ziegler-Natta catalyst. The polybutadiene rubber (PBR) having different *cis* content and molecular weight was obtained. The catalyst components included neodymium versatate ($NdV_3$) as catalyst, triethyl aluminum (TEAL) as cocatalyst or activator, and ethylaluminum sesquichloride (EASC) as chloride donor. For the modeling, three independent variables, namely monomer concentration (8-28 wt%), reaction time (1.5-2.5 h), and reaction temperature (45-75ºC) at three levels were selected to optimize the dependent variables or responses including monomer conversion, viscosity-average molecular weight and the *cis* isomer content of the obtained polymer. The interaction between three crucial parameters was studied and modeled. Quadratic models were obtained to relate process conditions to dependent variables. It was observed that the optimal conditions predicted by RSM were consistent with the experimental data. Statistical analysis demonstrated that concentration of the monomer and the time of reaction significantly affected *cis* content. Moreover, processing conditions to achieve the desired response variables were predicted and experimentally approved. The optimal reaction conditions derived from RSM are monomer concentration = 19 wt%, polymerization time = 2 hours, and polymerization temperature = 50ºC. Polymerization was carried out at optimum conditions. The appropriate level of dependent variables including 94.2% monomer conversion, 151812 g/mol viscosity-average molecular weight and 98.8% *cis* content was acquired. **Polyolefins J (2021) 8: 63-72**

**Keywords:** Ziegler-Natta, polybutadiene rubber, processing conditions, neodymium versatate, response surface method.

## INTRODUCTION

Polybutadiene rubber (PBR) can be synthesized by employing different approaches such as coordination polymerization and (controlled) radical polymerization [1-3]. Ziegler-Natta catalysts have been considerably employed for many years in the polymer industry as well as for the synthesis of PBR. Neodymium (Nd) catalysts are efficient systems in the *cis* polymerization of dienes monomers. Using neodymium-based catalysts higher *cis* content is achieved (≥ 98%) [4-6]. None of the catalytic systems classified previously (for example cobalt-based, titanium-based and nickel-based catalysts) for the *cis* polymerization of diene monomers indicates this characteristic [7]. Also, Nd-based catalyst causes the high activity of butadiene (Bd) polymerization and provides a homogeneous catalyst soluble in non-polar solvents such as n-hexane to give PBR with low gel (or insoluble polymer) content [8]. The high *cis*-PBR obtained using Nd catalyst exhibits attractive elastomeric properties and is particularly suitable for the tire industry [9-12].

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Since optimal processing conditions are very important in experimental works, traditionally, the trial and error approach is used to optimize processing conditions. In this method, only one parameter is altered, while the other parameters are kept constant. This optimization approach is named one-parameter at a time. This technique does not consider the interaction of parameters which is the major disadvantage of this method [13-15]. The single and mutual effects of various variables influencing the quantity and quality of the final product can be determined by design of experiment (DOE) which is a solution of the previous technique and an approved statistical approach in the research experimentations [15,16]. Response surface method (RSM) is an approach that has been widely used for designing of experiment that helps researchers to make models as regression equations for investigating interrelations between inputs and outputs and also to study effects of various variables or factors to achieve optimum conditions for desirable responses or results and also to decrease the quantity of required experimental runs to achieve statistically approved results [17,18]. For polymerization of propylene using Ziegler-Natta catalyst systems, RSM was used to evaluate and optimize operational variables such as the temperature, pressure, hydrogen volume and co-catalyst to catalyst ratio to achieve optimum activity of catalyst and MFR (melt flow rate). In other words, the optimum operating conditions were determined based on the optimization of the process cost [19, 20].The motivation of this research project stems from the need for more efficient operations of butadiene polymerization in a batch reactor. To achieve this goal, the technique of finding an optimum formulation is used.

In this work, the production process of polybutadiene rubber on a laboratory scale with high *cis* content was studied in which a three-component catalyst system containing neodymium versatate ($NdV_3$) as catalyst, triethylaluminum (TEAL) as cocatalyst or activator and ethylaluminum sesquichloride (EASC) as a chloride donor was used for solution polymerization of butadiene monomer. Systematic study was done to evaluate the influence of independent variables (monomer concentration, reaction time and reaction temperature) on dependent variables or responses including monomer conversion, molecular weight and *cis* content of the obtained polymer. For this purpose RSM with central composite design (CCD) was used. This method helped to determine whether there is a synergistic influence of polymerization conditions on the polymerization and final properties of polymer or not. Moreover, regression models through RSM was reported regarding the development of monomer conversion, molecular weight, and *cis* content in coordination polymerization of butadiene monomer. Also, optimum processing parameters are determined for maximum dependent variables.

## EXPERIMENTAL SECTION

### Materials

n-Hexane (industrial grade, Shazand Petrochemical Company, Iran) was dried before use by passing through two columns filled with molecular sieves (4Å) resulting in residual water content of 10 ppm. 1,3-Butadiene monomer (polymerization grade, Tabriz Petrochemical Company, Iran), neodymium versatate ($NdV_3$, Ningbo Finchem Company, China, 0.3 M solution in n-hexane), triethylaluminum (TEAL, Sigma-Aldrich, 5.5 M in n-hexane), and ethylaluminum sesquichloride (EASC, Sigma-Aldrich, 1.1 M in n-hexane) were used as received without further purification.

### Polymerization procedure

The polymerization reactions were performed in a 1 liter stainless steel reactor (Buchi AG, Switzerland) equipped with a jacket, mechanical stirrer and temperature as well as pressure indicators. The reactor was purged with high-purity nitrogen to remove moisture and air in such a way that the reactor was filled with nitrogen and heated to 100°C and discharged after 10 minutes several times. Before begining, the reactor was cooled to the desired reaction temperature, while it was kept under a nitrogen purge. Then, the reactor was filled with nearly 500 ml of n-hexane. After that, TEAL was injected into the reactor and then after 10 minutes, $NdV_3$ and EASC were added, and immediately butadiene was entered with a desired flow rate. Once the reaction was completed, the unreacted monomer was discharged and 10 ml of acidified ethanol (HCl, 5 wt%) was injected to stop the polymerization and deactivate the catalyst. The resulted polymer was washed with alcohol and hexane and then the polymer was filtered and dried in vacuo for 2 hours at 75°C.

### Characterizations

The microstructure of polybutadiene was investigated by Fourier-transform infrared (FT-IR) spectroscopy

**Table 1**. Independent factors and their coded level in RSM.

| Variables | Notation | Low level (-1) | Mean level (0) | High level (+1) |
|---|---|---|---|---|
| **Monomer conc. (*wt.* %)** | A | 8 | 18 | 28 |
| **Reaction time (h)** | B | 1.5 | 2.0 | 2.5 |
| **Reaction temp. (°C)** | C | 45 | 60 | 75 |

from 400 to 4000 $cm^{-1}$ using FTIR-8900 (Shimadzu). The isomers contents were obtained using the absorbances at 740 $cm^{-1}$ (*cis*), 910 $cm^{-1}$ (vinyl-1,2) and 965 $cm^{-1}$ (*trans*). In this study, the FTIR peaks were deconvoluted using PeakFit software (version 4.12) and then the area below the specific peaks was calculated and the content of each isomer was reported. The conversion of monomer was calculated by gravimetric analysis. After completion of the polymerization reactions, samples were taken. The weight of the samples was determined after deactivation of the catalyst by adding 10 ml of acidic ethanol solution (HCl, 5% wt.) and removing the residual butadiene and solvent by drying in vacuo at 75 °C for 2 hours. The degree of reaction conversion was calculated by Equation (1):

$$Conversion\ (\%) = \frac{mass\ of\ \ polymer\ obtained}{monomer\ mass\ \ fed\ to\ the\ reactor} \times 100 \tag{1}$$

The viscosity-average molecular weight was determined from measuring the intrinsic viscosity ([η]) of diluted solutions of polybutadiene rubber in toluene by Proline PVS 15-Lauda and using the Mark-Houwink's equation (Equation 2):

$$[\eta] = k.\overline{\mathrm{M}}_{\mathrm{v}}{}^{a} \tag{2}$$

where $\overline{\mathrm{M}}_{\mathrm{v}}$ is the viscosity-average molecular weight. Also *k* and *a* are Mark-Houwink's constants for toluene at 25ºC, which are 0.000305 dL/g and 0.725, respectively [21].

**Experimental design and statistical analysis via RSM**

RSM was used to design experiments and evaluate the effects of the parameters. To design the response surface experiment, the type of design, the number of factors or independent variables, the names of the factors, their high and low levels and replication points must be entered in the design software. To perform statistical analysis and development of regression models, central composite experimental design (CCD) established via Design Expert software (7.1.6 trial version) was used. Independent variables in this study included three factors: A: monomer concentration (wt. %), B: time of reaction (hours) and C: temperature (ºC) of reaction. The levels of these factors and the ratios of the catalyst components have been selected based on the knowledge obtained from our previous studies [21] with the same catalytic system used. The levels of the independent variables are listed in Table 1. It should be noted that in the previous study, 15 experiments were performed to optimize the molar ratios of catalyst components [21]. Dependent variables or responses were monomer

**Table 2**. Central composite design layout and corresponding results.

| Run | Monomer conc. (*wt.* %) | Reaction time (h) | Reaction temp. (˚C) | Conversion (%) | $\overline{M}_v$ (g/mol) | *cis*-1,4 (%) |
|---|---|---|---|---|---|---|
| **1** | 8 | 1.5 | 45 | 42.0 | 110821 | 94.0 |
| **2** | 8 | 1.5 | 75 | 33.0 | 102110 | 94.0 |
| **3** | 8 | 2.0 | 60 | 81.0 | 113921 | 97.0 |
| **4** | 8 | 2.5 | 45 | 78.0 | 107423 | 96.0 |
| **5** | 8 | 2.5 | 75 | 36.0 | 98829 | 94.0 |
| **6** | 18 | 1.5 | 60 | 75.0 | 123701 | 95.0 |
| **7** | 18 | 2.0 | 45 | 80.0 | 176192 | 98.0 |
| **8** | 18 | 2.0 | 60 | 98.0 | 145117 | 99.0 |
| **9** | 18 | 2.0 | 75 | 73.0 | 148296 | 98.0 |
| **10** | 18 | 2.5 | 60 | 97.4 | 146237 | 98.0 |
| **11** | 28 | 1.5 | 45 | 58.0 | 101297 | 95.0 |
| **12** | 28 | 1.5 | 75 | 36.0 | 115011 | 95.0 |
| **13** | 28 | 2.0 | 60 | 96.0 | 151219 | 98.0 |
| **14** | 28 | 2.5 | 45 | 45.0 | 117439 | 96.0 |
| **15** | 28 | 2.5 | 75 | 28.0 | 91774 | 97.0 |

$[NdV_3]$ = 0.40 mmol/lit, [Bd]/[Nd] = 5363.0, [Al]/[Nd] = 27.2, [Cl]/[Nd] = 2.2

conversion, viscosity-average molecular weight and *cis* content of the resulted polymer. Experiments were performed based on the designed matrix. Accordingly, Table 2 shows the test design and the actual responses of the experiments performed in this study.

## RESULTS AND DISCUSSION

### Statistical analysis of experimental data

To evaluate the quality of developed models, $R^2$ (coefficients of determination) was used and to statistically understand the models, analysis of variance (ANOVA) was performed. ANOVA is a set of methods for comparing several means in different groups [20]. The ANOVA table demonstrates the significance of first-order, second-order and cross-product terms of polynomial equations. The quadratic equations with good acceptability of fitting for monomer conversion, viscosity-average molecular weight and *cis* content were developed as shown in Equations 3 - 5, respectively:

$$Conv. = 101.80 - 0.70\times A + 4.04\times B - 9.70\times C - 7.50\times A \times B + 1.5\times A\times C - 3.50\times B\times C - 14.26\times A^2 - 16.56\times B^2 - 26.26\times C^2 \quad (3)$$

$$\bar{M}_v = 157200 + 4363.60\times A + 876.20\times B - 5715.20\times C - 52.00\times A\times B + 669.25\times A\times C - 4907.75\times B\times C - 27640.78\times A^2 - 25241.78\times B^2 + 2033.22\times C^2 \quad (4)$$

$$Cis\ \text{content} = 98.60 + 0.60\times A + 0.80\times B - 0.10\times C + 0.13\times A\times B + 0.38\times A\times C - 0.12\times B\times C - 1.00\times A^2 - 2.00\times B^2 - 0.50\times C^2 \quad (5)$$

For all models a good coefficient of determination was observed. $R^2$ value for Equations 3-5 are 0.934, 0.938 and 0.936, respectively. If the value of $R^2$ approaching to unity (1.000), the model predicts response value adjacent to the actual one. This indicates that quadratic polynomial models were sufficient and satisfactorily correlate responses (dependent variables) with significant independent variables.

ANOVA has been presented in Table 3. The positive symbol (+) shows synergistic influence whereas the negative one (–) indicates the opposed effect. Examining the corresponding probability value (P) of each parameter determines its importance [22]. The low value of P indicates the importance of the effect of the relevant coefficient and also its role on the dependent variables [13]. The model parameters are significant when P values are lower than 0.0500, and statistically insignificant if the P values are greater than 0.0500 [23]. Therefore, in the regression model related to monomer conversion, there are two significant parameters “C” and “$C^2$”, in the regression model related to viscosity-average molecular weight, only one significant parameter, “$A^2$”, exists and in the regression model related to *cis* content, A, B and $B^2$ are significant parameters. It is worth noting that the parameters AB, AC and BC do not affect the dependent variables. However, an analysis must be performed to evaluate whether the model validates the experimental data. Therefore, the analysis here involves determining the squared value of R, $R^2$, as shown previously. In addition, the adequacy of the model is assessed using a residual survey. The differences between the observed and the predicted responses are the residuals that are examined through the normal probability plots of the residuals. The model is very appropriate if the points in the normal probability plots form a straight line, which confirms the adequacy of fitting of the regression models. Figure 1 shows the normal probability plots of the residuals.

It is worth mentioning that the color points for all the Figures are the same as Figure 1. The plots indicate that generally the residuals placed on a straight

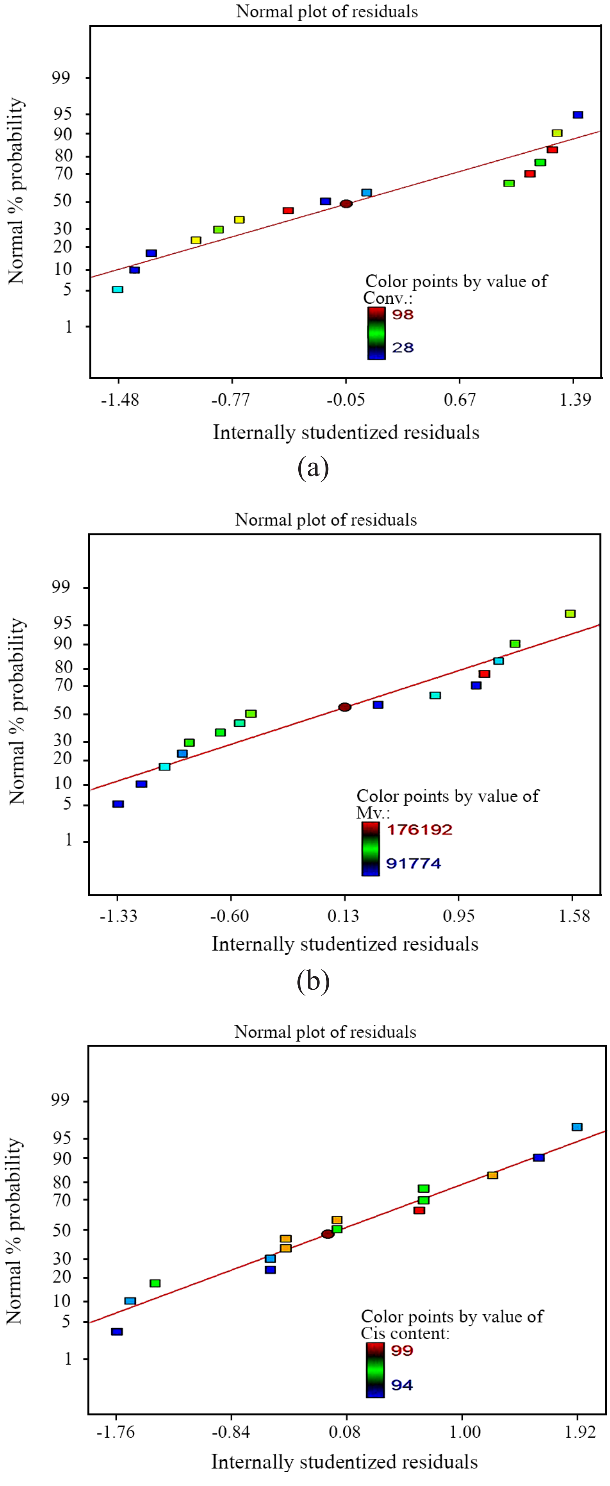
**Table 3**. ANOVA for response surface models.

| Terms of the models | P* value for conversion | P value for molecular weight | P value for *cis* content |
|---|---|---|---|
| **A: Monomer conc.** | 0.8470 | 0.4393 | 0.0472 |
| **B: Reaction time** | 0.2937 | 0.8727 | 0.0174 |
| **C: Reaction temp.** | 0.0373 | 0.3214 | 0.6807 |
| **AB** | 0.1090 | 0.9932 | 0.6462 |
| **AC** | 0.7129 | 0.9128 | 0.2031 |
| **BC** | 0.4051 | 0.4367 | 0.6462 |
| **$A^2$** | 0.0899 | 0.0429 | 0.0778 |
| **$B^2$** | 0.0588 | 0.0570 | 0.0069 |
| **$C^2$** | 0.0118 | 0.8505 | 0.3189 |

* Probability value

line showing normal distribution of the errors. Additionally, Figure 2 shows the differences between actual (from experminent) and predicted (from quadratic models) response values.

Based on the obtained results, it can be concluded that the predicted values are fairly close to the actual ones. The model equations obtained from RSM could be used satisfactorily to determine the dependent variables over a wide range of polymerization conditions.

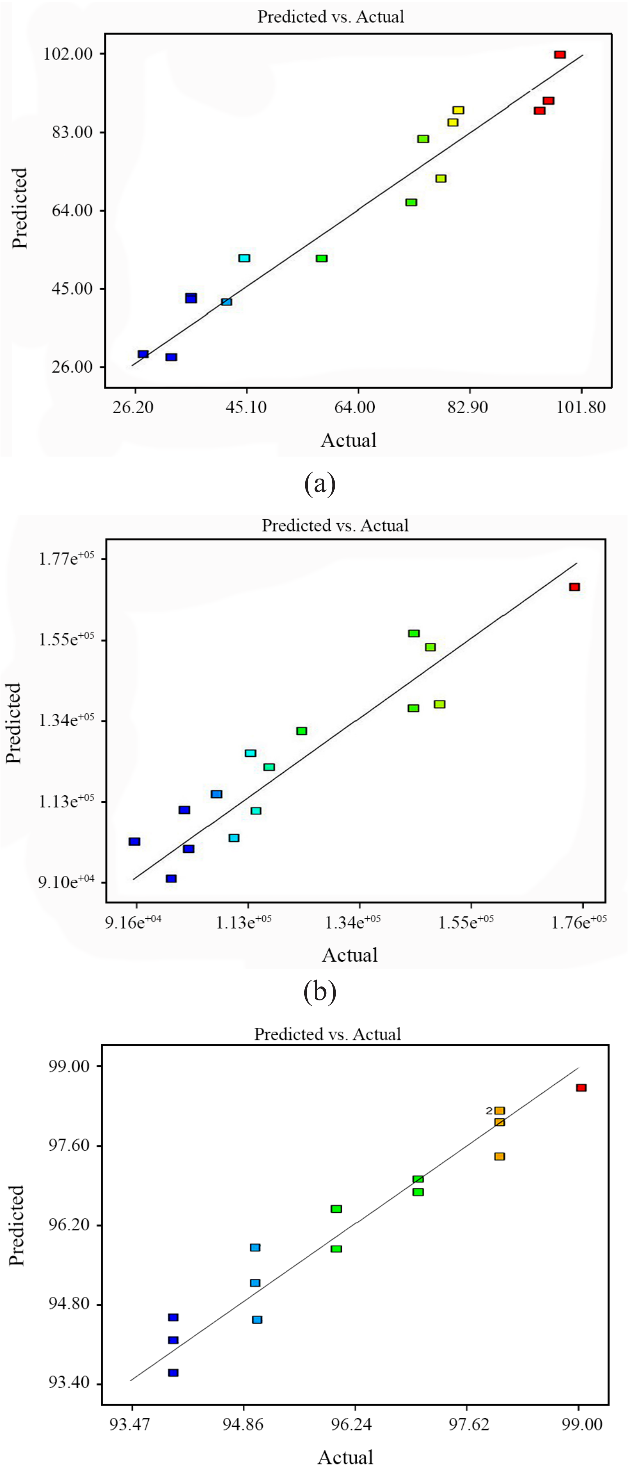


(a)

(b)

(c)

**Figure 1**. Normal probability plots of residuals of (a) monomer conversion, (b) molecular weight and (c) *cis* content.



(a)

(b)

(c)

**Figure 2**. Diagrams of comparison between the predicted and actual values of (a) monomer conversion, (b) molecular weight and (c) *cis* content.

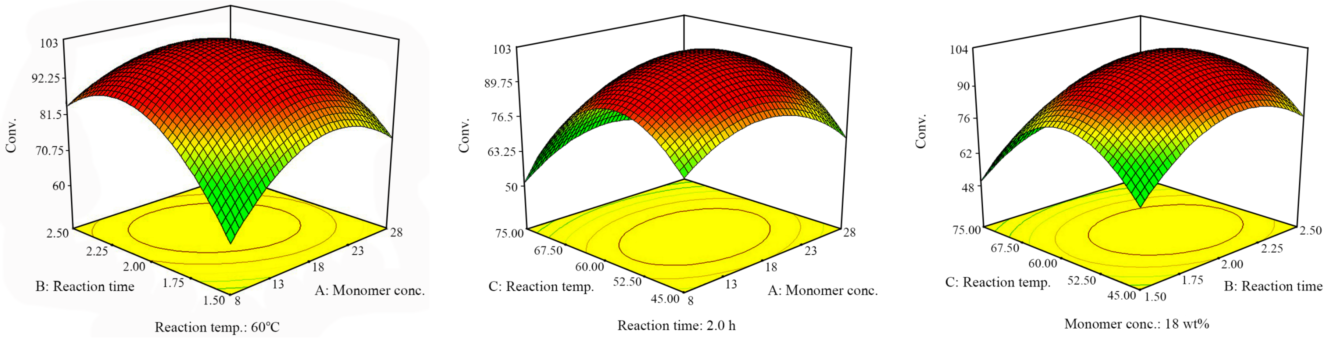
## Effect of independent parameters on monomer conversion

One of the main differences between the PBR production licenses is the temperatures employed in the polymerization reactors to achieve a high-quality product. It is well-known that the polymerization reaction temperature is crucial for dienes polymerization and has a special and strong influence on polymerization rate and monomer conversion using the Nd-based Ziegler-Natta catalyst to reach high activity [24]. The relevant results of changing the reaction temperature are listed in Table 2. Figure 3 shows the relationship between monomer conversion and monomer concentration, reaction time and reaction temperature where in each graph a variable was kept constant at mean value. The plots related to the monomer conversion response are more similar to a semispherical shape which show clearly, the optimum conditions to achieve maximum response value. It can be observed from the semispherical response surface of the monomer conversion (Figures 3-b and 3-c). The polymerization reaction rate or monomer conversion remarkably is influenced by the polymerization reaction temperature. Besides, as the reaction temperature reaches a certain level the rate of polymerization reaction raises.

These figures propose that there is an optimum temperature. As temperature rises above the optimum value, monomer conversion reduces due to thermal decomposition [1,12,25]. Also at temperatures lower than optimum value, induction time and activation of the catalyst system result in lower monomer conversion. This behavior is attributed to the reduction of the propagation rate constant at lower polymerization temperatures [1]. To illuminate the effects of monomer concentration on the polymerization solvent, the monomer concentration was varied between 8 and 28 wt. %. The effect of variation of monomer concentration on the dependent variables was studied perceptibly. As can be seen from Figures 3-a and 3-b, the monomer conversion shows a maximum point at 20 wt. % (approximately) of monomer concentration. At higher monomer concentration, above 20 wt. %, the decrease of butadiene monomer is observed which might be described by the chain transfer reactions to butadiene monomer. This results in a lower polymerization rate and monomer conversion.

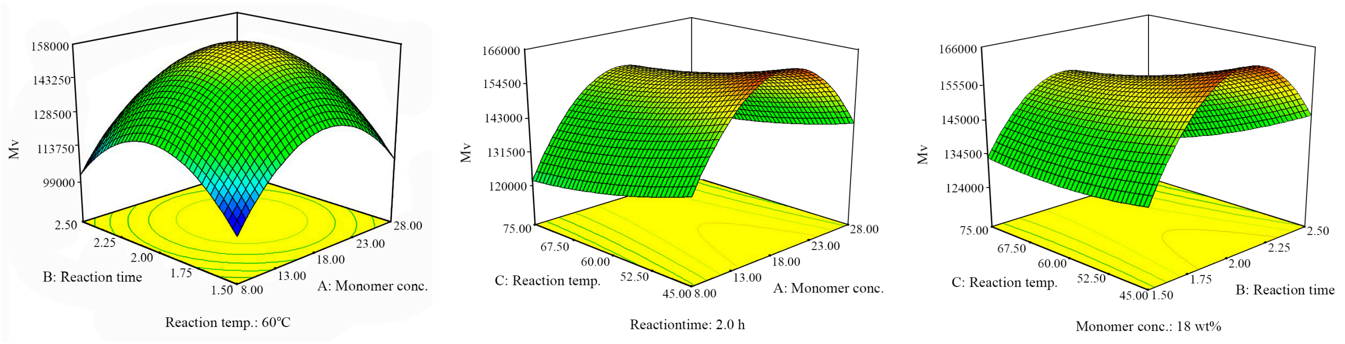
## Effect of independent parameters on viscosity-average molecular weight

Figure 4 shows the relations of viscosity-average molecular weight with monomer concentration, reaction time, and reaction temperature. From Figures 4-b and 4-c which are dome-shaped surface plots of molecular weight, little change of the molecular weight by increasing reaction temperature is noticeable. In these cases, in one axis, there is a linear increase or decrease in molecular weight while in the other axis there is an increase in the molecular weight only up to a certain extent and it decreases thereafter. Indeed, it is anticipated that an increase in temperature should lead to a reduction in molecular weight. However, a temperature rise may result in branching, causing a molecular weight increase [1]. It can be expected from Figure 4-c that the monomer concentration is equal or very close to the optimum value where the molecular weight is approximately constant without any chain transfer reaction to the monomer [26]. It is worth noting that by increasing reaction time (Figures 4-a and 4-c) the concentration of active sites decreases. Thus, the monomer conversion and molecular weight decrease because TEAL acts as a transfer agent. Also, when the amount of butadiene monomer (Figures 4-a



(a) (b) (c)

**Figure 3**. Surface plots of monomer conversion (%) as a function of (a) reaction temperature, (b) reaction time and (c) monomer oncentration.



(a) (b) (c)

**Figure 4**. Surface plots of viscosity-average molecular weight (g/mol) as a function of (a) reaction temperature, (b) reaction time and (c) monomer concentration.

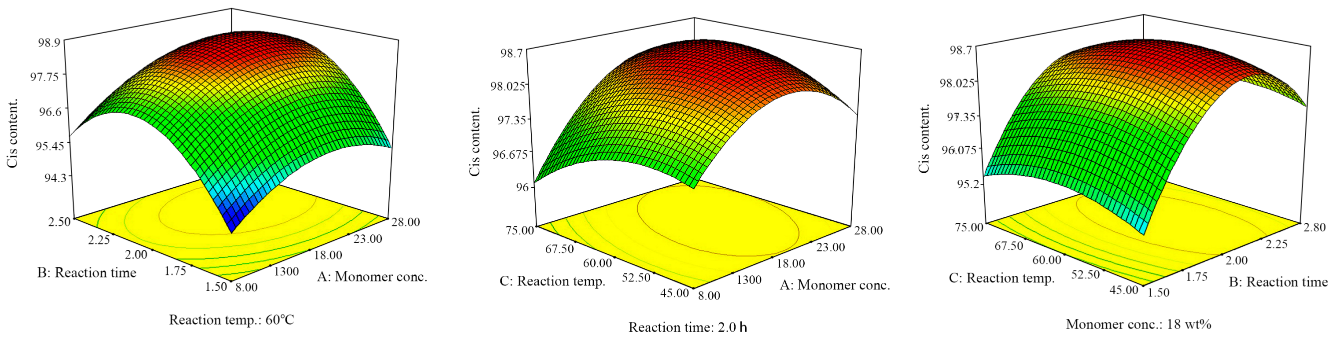
and b) was increased to about 18 wt. %, the molecular weight increased and then, due to chain transfer reactions to monomer, decreased [27].

## Effect of independent parameters on *cis* content

Figure 5 shows *cis* content responses to variation in monomer concentration, reaction time and reaction temperature. Interestingly, it can be seen that the *cis* content was increased by increasing the monomer concentration until an optimum value (Figures 5-a and 5-b). After the optimum value point, the cis content reduced due to the higher movability of monomer molecules originated from lower or appropriate solution viscosity of reaction media; thus, monomer inserting will happen to the catalyst sites in the opportune configuration [1,28]. Besides, the microstructure of the resulting PBR is influenced as polymerization temperature varies. It is worth noting that the *cis* content decreases by increasing of polymerization reaction temperature after a temperature optimum value (Figures 5-b and 5-c). This finding also is confirmed by Oehme et al. [29] and Enriquez-Medrano et al. [30]. Polymers synthesized at higher temperatures show fairly low *cis* content because at higher reaction temperature *cis* to *trans* isomerization is accelerated [27,29].

## Optimization of independent parameters

The Design Expert software provides a possibility to determine a process condition to have a product with the desirable specification. It provides an approach to identify the combination of input variable settings that jointly optimize a set of responses. The goal for the program should be chosen from five possibilities: namely “maximize”, “minimize”, “target”, “in range” and “equal to”, for an objective [31]. To predict the optimum independent variables, it needs to introduce a desirable range of the dependent parameters to the software then arranges the experimental condition along with predicted values for the responses. The final goal of this optimization was to, simultaneously, gain the maximum level for all dependent variables, namely the monomer conversion, molecular weight, and *cis* content. Accordingly, the best software run was selected as shown in Table 4 since it had the highest desirability, 0.912. The desirability can change from zero to one for any given response. In an ideal



(a) (b) (c)

**Figure 5**. Surface plots of *cis* content (%) as a function of (a) reaction temperature, (b) reaction time and (c) monomer concentration.

**Table 4**. Optimal independent variables and their predicted responses.

| Independent variables | | | Predicted dependent variables | | |
|---|---|---|---|---|---|
| Monomer conc. (*wt.* %) | Reaction time (h) | Reaction temp. (˚C) | Conversion (%) | $M_v$ (g/mol) | *Cis* content (%) |
| 19.0 | 2.0 | 50 | 98.0 | 161524 | 98.6 |

**Table 5**. Results of validated experiments conducted at optimum conditions.

| Dependent variables | Predicted value | Experimental value (average of two runs) | Error (%) |
|---|---|---|---|
| **Monomer conv. (%)** | 98.0 | 94.2 | 3.9 |
| **Molecular weight (g/mol)** | 161524 | 151812 | 6.0 |
| ***cis* content (%)** | 98.6 | 98.8 | 0.2 |

case the value is one while the zero shows that one or more responses fall outside of the desirable ranges. The obtained desirability of about 0.912 is rather close to the ideal one.

The independent parameters which were suggested by software, were examined experimentally, to evaluate their values as well as related errors. Table 5 gives a comparison between the predicted and experimental values. The related errors for conversion of monomer, average molecular weight, and *cis* content are 3.9, 6.0, and 0.2 %, respectively, which are quite small. These results indicate that the used model (for three regression models) to predict the responses has good accuracy and reliability.

## CONCLUSION

The purpose of this research was to optimize the processing parameters: concentration of monomer, time of polymerization and reaction temperature of butadiene polymerization using Ziegler-Natta catalyst based on neodymium metal in n-hexane solvent. The response surface method (RSM) was successfully used to optimize the processing conditions regarding the conversion of monomer, viscosity-average molecular weight, and *cis* isomer content as dependent variables or responses. Three quadratic experimental models were obtained to simulate the dependent variables in terms of operational conditions by central composite design (CCD) with adequate goodness of fit and an ANOVA test was performed. The quadratic models developed using RSM were reasonably accurate and could be used to predict the dependent variables within the range of the investigated parameters. The evaluation of correlation coefficient for the experimental models was quite satisfactory. The statistical analysis of the results showed that monomer concentration and time of reaction significantly affected *cis* content of the resulting polymer. Moreover, the optimum values for concentration of monomer, time and temperature of reaction were found to be 19.0 wt. %, 2.0 h, and 50°C, respectively, that were well predicted by software in which the desirable responses were obtained.

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**Conflict of interest**: The authors declare that they have no conflict of interest.

**Data availability**: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

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