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Modelling of the butadiene and isoprene polymerization processes with a binary neodymium-based catalyst

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Abstract

In the present work we study the mechanism of the polymerization processes of isoprene and butadiene with the $NdCl_3{\cdot}3TBP$–TIBA catalyst system (TBP = tributylphosphate, TIBA = triisobutylaluminium) using two mathematical models: one which takes into account a monomolecular termination and the other which considers that no termination reactions occur during the polymerization process. Both for isoprene and butadiene, by comparing with the experimental data, the best results were achieved from the equations derived in the frame of the polymerization model considering the absence of the termination reactions. The product between the rate constant of the propagation reaction and the active centres concentration depends mainly on the [Al]/[Nd] molar ratio used which is an argument for the participation of TIBA in the formation of the active centres. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Ziegler–Natta catalysts have been used extensively for many years for the production of polybutadienes and polyisoprenes, particularly where high 1,4-*cis* contents are required [1]. More recently, the use of lanthanide coordination catalysts has permitted higher degrees of stereoregulation to be achieved; for example, neodymium based systems have been shown to be particularly effective in producing polybutadienes and polyisoprenes with 1,4-*cis* contents of about 97% and 95%, respectively [2, 3]. Studies in our laboratory with a $NdCl_3{\cdot}3L\text{-}AlR_3$ catalyst system have produced polyisoprenes with even higher 1,4-*cis* levels [4, 5].

Very few data in connection with the modelling of this process are reported in the literature. Only a paper by Pross [6] revealed information about the modelling of the polymerization process of butadiene with a ternary neodymium-based catalyst system, assuming that the polymerization process is governed by a "living" mechanism.

A detailed study regarding modelling and simulation of the polymerization process of butadiene and isoprene with $NdCl_3{\cdot}3L\text{-}AlR_3$ catalyst system (L = tributylphosphat, R = isobutyl) is reported in this paper. On the basis of the obtained data, some kinetic parameters are calculated and conclusions concerning the polymerization mechanism are drawn.

In order to evaluate the mechanism of the stereospecific polymerization process of butadiene and isoprene with $NdCl_3{\cdot}3TBP$–TIBA (TBP = tributylphosphat, TIBA = triisobutylaluminum) catalyst system, two mathematical models are developed, the first one taking into account the termination reactions to occur and the second one considering the absence of any termination reactions.

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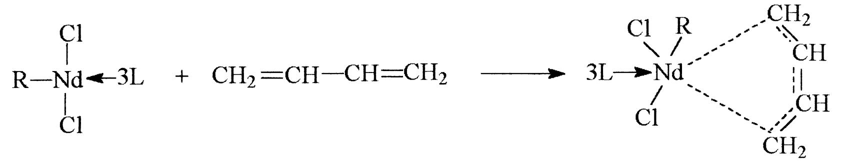
2. Theoretical

2.1. Polymerization mechanism

Firstly it was assumed that the following reactions might occur during the polymerization process:

2.1.1. Initiation

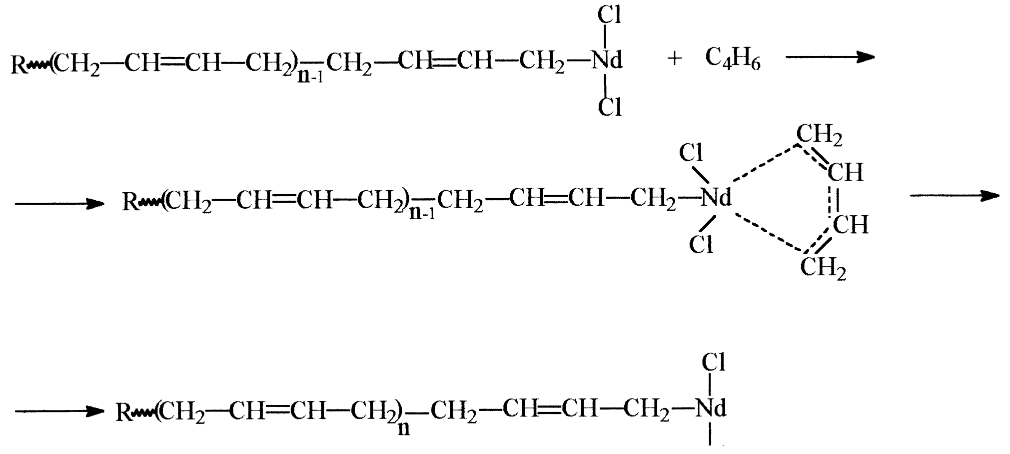
$$NdCL_3 \cdot 3L + AlR_3 \rightarrow RNdCl_2 \cdot 3L + AlR_2Cl \quad (1)$$



$$RNdCl_2 \leftarrow 3L + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow 3L \rightarrow Nd(Cl)_2R(\eta\text{-}CH_2{=}CH{-}CH{=}CH_2) \quad (2)$$

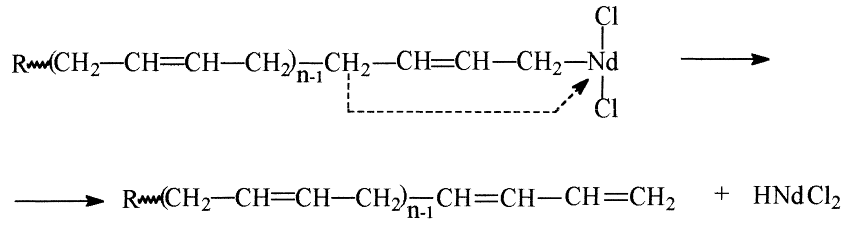
The second reaction is possible due to the high number of coordination possibilities at the neodymium atom through the vacancies on its "4f" orbitals. In the following reactions the three molecules of ligand (L) will not be any more shown, understanding that they always coordinate with the neodymium atom, contributing to its stability.

2.1.2. Propagation



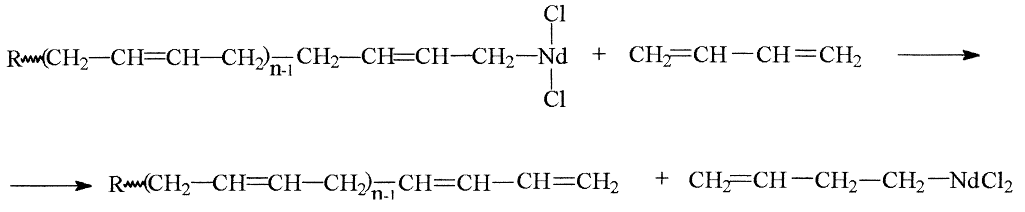
$$R{\sim\sim}(CH_2{-}CH{=}CH{-}CH_2)_{n-1}{-}CH_2{-}CH{=}CH{-}CH_2{-}NdCl_2 + C_4H_6 \longrightarrow R{\sim\sim}(CH_2{-}CH{=}CH{-}CH_2)_{n-1}{-}CH_2{-}CH{=}CH{-}CH_2{-}NdCl_2(C_4H_6) \longrightarrow R{\sim\sim}(CH_2{-}CH{=}CH{-}CH_2)_{n}{-}CH_2{-}CH{=}CH{-}CH_2{-}NdCl \quad (3)$$

2.1.3. Monomolecular termination



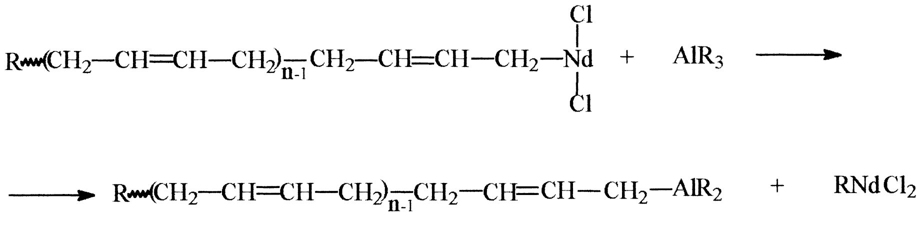
$$R{\sim\sim}(CH_2{-}CH{=}CH{-}CH_2)_{n-1}{-}CH_2{-}CH{=}CH{-}CH_2{-}NdCl_2 \longrightarrow R{\sim\sim}(CH_2{-}CH{=}CH{-}CH_2)_{n-1}{-}CH{=}CH{-}CH{=}CH_2 + HNdCl_2 \quad (4)$$

2.1.4. Transfer to the monomer



$$R{\sim\sim}(CH_2{-}CH{=}CH{-}CH_2)_{n-1}{-}CH_2{-}CH{=}CH{-}CH_2{-}NdCl_2 + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow R{\sim\sim}(CH_2{-}CH{=}CH{-}CH_2)_{n-1}{-}CH{=}CH{-}CH{=}CH_2 + CH_2{=}CH{-}CH_2{-}CH_2{-}NdCl_2 \quad (5)$$

2.1.5. Transfer to the organoaluminum compound



$$R\sim(CH_2{-}CH{=}CH{-}CH_2)_{n-1}{-}CH_2{-}CH{=}CH{-}CH_2{-}\underset{Cl}{\overset{Cl}{Nd}} + AlR_3 \longrightarrow$$

$$\longrightarrow R\sim(CH_2{-}CH{=}CH{-}CH_2)_{n-1}{-}CH_2{-}CH{=}CH{-}CH_2{-}AlR_2 + RNdCl_2 \qquad (6)$$

The possibility of chain transfer reaction with the solvent is excluded because aliphatic hydrocarbons (*n*-hexane was used) are not chain transfer agents on polymerization of the dienes with lanthanide catalysts [7].

2.2. Mathematical modelling

The polymerization process may be kinetically described by the equations of monomer consuming and active centres consuming, respectively:

$$-\frac{dC}{dt} = k_1 \cdot C \qquad (7)$$

$$-\frac{dM}{dt} = k_c \cdot C \cdot M \qquad (8)$$

with the boundary condition: at $t = 0$:

$$C = C_0 \qquad (9)$$

$$M = M_0 \qquad (10)$$

where C = the active centres concentration (mol/l); M = the monomer concentration (mol/l); t = polymerization time (min); k_1 = the constant rate of the monomolecular termination reaction (min^{-1}); k_c = the constant rate of the propagation reaction (l/mol min).

Two possibilities will be considered, deriving from Eqs. (7) and (8):

$$\text{(a) Monomolecular termination}: k_1 > 0 \qquad (11)$$

$$\text{(b) The absence of termination reactions}: k_1 = 0. \qquad (12)$$

Each of these cases is analysed by developing a complete model.

2.2.1. (a) Monomolecular termination

Inserting condition (11) into Eqs. (7) and (8), one finds:

$$-\frac{dC}{dt} = k_1 C \qquad (13)$$

$$-\frac{dM}{dt} = k_c \cdot C \cdot M. \qquad (14)$$

By integration of Eq. (13) using boundary condition (9), we obtain:

$$C = C_0 \exp(-k_1 \cdot t). \qquad (15)$$

Inserting Eq. (15) in Eq. (14) one finds:

$$-\frac{dM}{dt} = (k_c \cdot C_0)\exp(-k_1 t) \cdot M \qquad (16)$$

which by integration leads to:

$$\ln\frac{M}{M_0} = \frac{k_c 0}{k_1} \cdot (\exp(-k_1 t) - 1). \qquad (17)$$

A quick verification for Eq. (16) in comparison with the experimental data may be carried out in the following way:

$$-\frac{dM}{dt} \cdot \frac{1}{M} = (k_c \cdot C_0)\exp(-k_1 \cdot t) \qquad (18)$$

and by logarithmation a linear equation is obtained:

$$\ln\left(-\frac{dM}{dt} \cdot \frac{1}{M}\right) = \ln(l_c \cdot C_0) - k_1 \cdot t. \qquad (19)$$

Defining:

$$y = \ln\left(-\frac{dM}{dt} \cdot \frac{1}{M}\right) \qquad (20)$$

$$a = \ln(k_c \cdot C_0) \qquad (21)$$

$$b = -k_1. \qquad (22)$$

We obtain:

$$y = a + b \cdot t. \qquad (23)$$

When working with the above equations, a difficult problem is to evaluate the derivative dM/dt from the experimental data. Therefore in order to avoid any possible numerical errors in calculating the derivatives, the following function was considered:

$$\phi_1(a', b') = \frac{1}{2}\sum_{i=1}^{n}\left\{\exp\left[\frac{a'}{b'}(\exp(-b' \cdot t_i) - 1)\right] - \frac{M_i}{M_{i0}}\right\}^2 \qquad (24)$$

where

$$a' = k_c \cdot C_0 \qquad (25)$$

$$b' = k_1. \tag{26}$$

The a' and b' constants may be determined from the following non-linear equations:

$$\frac{\partial \phi_1}{\partial a'} = 0 \tag{27}$$

$$\frac{\partial \phi_1}{\partial b'} = 0. \tag{28}$$

Due to the fact that the experimental data sets correspond to different catalyst concentrations but at the same temperature, a generalization of the function (24) is:

$$\begin{aligned}\phi_2(a_2', a_2', \ldots, a_m', b') &= \frac{1}{2}\sum_{i=1}^{n_1}\left\{\exp\left[\frac{a_1'}{b'}(\exp(-b' \cdot t_{i1}) - 1)\right] - \frac{M_{i1}}{M_{i1,0}}\right\}^2 \\ &+ \frac{1}{2}\sum_{i=1}^{n_2}\left\{\exp\left[\frac{a_2'}{b'}(\exp(-b' \cdot t_{i2}) - 1)\right] - \frac{M_{i2}}{M_{i2,0}}\right\}^2 \\ &+ \cdots + \frac{1}{2}\sum_{i=1}^{n_m}\left\{\exp\left[\frac{a_m'}{b'}(\exp(-b' \cdot t_{im}) - 1)\right] - \frac{M_{im}}{M_{im,0}}\right\}^2.\end{aligned} \tag{29}$$

By minimizing the function (29) the values of the constantsa'_i, $i = 1,\ldots,m$ and constant b' are obtained.

In Eq. (29): n_i ($i = 1,\ldots,m$) is the number of experimental data from the set "i" and the constants a'_i are given by the expression:

$$k_c \cdot C_{0i} = a_i'. \tag{30}$$

By minimizing the function (29) the information is extracted from all experimental data sets which are simultaneously analysed.

Minimizing the function (29) is equivalent with solving the non-linear system:

$$\frac{\partial \phi_2}{\partial a_i'}(a_1', \ldots, a_m', b') = 0 \tag{31}$$

$$\frac{\partial \phi_2}{\partial b_i'}(a_1', \ldots, a_m', b') = 0. \tag{32}$$

2.2.2. (b) The absence of termination reactions

Inserting condition (12) into Eqs. (7) and (8), one finds:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = 0 \tag{33}$$

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = k_c \cdot C \cdot M. \tag{34}$$

In this case the concentration of the active centres is constant but Eqs. (33) and (34) do not exclude the possibility of the transfer reactions to occur.

By integrating Eq. (33) with the boundary condition (9) one finds:

$$C = C_0$$

and substituting in Eq. (34) we obtain by integration:

$$\ln\frac{M}{M_0} = -k_c \cdot C_0 \cdot t. \tag{35}$$

Using as co-ordinates ln M/M_0 and time (t), Eq. (35) represents a line, which passes through the origin:

$$y = \ln\frac{M}{M_0} \tag{36}$$

$$y = a'' \cdot t \tag{37}$$

where $a'' = -k_c \cdot C_0$.

The value of constant a'' may be calculated by minimization the following function:

$$\phi(a'') = \frac{1}{2}\sum_{i=1}^{n}(a'' \cdot t_i - y_i)^2 \tag{38}$$

which is equivalent in Gauss notations with:

$$a'' = \frac{[yt]}{[t^2]}. \tag{39}$$

For each mathematical model presented above and on the basis of the kinetic equations derived, the theoretical values of the monomer concentration ($[M]$) at any time of reaction were calculated using a programme written in Pascal and run on a PC. Moreover the errors against the experimental data were determined.

3. Experimental

The experimental data were obtained for the polymerization processes of butadiene and isoprene using the $NdCl_3 \cdot 3TBP$–TIBA catalyst system, carrying out six sets of experiments for each monomer in the conditions presented in Table 1.

3.1. Materials

n-Hexane used as the polymerization solvent was supplied by Merck and was distilled onto Na–K alloy and purified according to a method we describe elsewhere [4]. The same solvent was used for the preparation of $NdCl_3 \cdot 3TBP$ and TIBA solutions.

Tributylphosphate (supplied by Merck) was purified by vacuum distillation and final traces of moisture

Table 1
The experimental conditions for the polymerization of isoprene and butadiene using the $NdCl_3 \cdot 3TBP$–TIBA catalyst system

No. of experiment	Monomer	Temperature (°C)	M_0 (mol/l)	$[Nd] \times 10^{+6}$ [mol/g diene]	[Al]/[Nd] molar ratio
1	Isoprene	30	3	4	20
2	Isoprene	30	3	4	30
3	Isoprene	30	3	4	40
4	Isoprene	30	3	4	60
5	Isoprene	30	3	4	100
6	Isoprene	30	3	2	30
1	Butadiene	30	1.5	4	20
2	Butadiene	30	1.5	4	30
3	Butadiene	30	1.5	4	40
4	Butadiene	30	1.5	4	60
5	Butadiene	30	1.5	4	100
6	Butadiene	30	1.5	2	30

removed by azeotropic distillation in a special apparatus [4].

The raw lanthanide material $NdCl_3 \cdot 6H_2O$ was used as supplied by the Research Institute for Special Metals, Romania, and $NdCl_3 \cdot 3TBP$ complexes (0.0328 mol/l) were obtained using our original method described in a previous paper [8].

Triisobutylaluminium (supplied by Merck) was diluted with *n*-hexane up to a concentration of 0.984 mol/l.

The 1,3-butadiene used was a high purity grade (acetylene content less than 50 ppm) supplied by CAROM, Onesti, Romania. The monomer was further purified by passing it through columns packed with NaOH and molecular sieves to remove any residual moisture and then through a column packed with copper to remove the last traces of acetylene. Prior to each polymerization, the butadiene was passed through a little column filled with TIBA. In order to dose the required amount of monomer, the butadiene was condensed under high vacuum in a cylinder-shaped glass vessel (3) made from a burette, by introducing liquid nitrogen as a condensing agent in the Dewar vessel (2) attached to (3) (Fig. 1). After the condensing, the vessel (3) was heated with a hair-dryer up to the room temperature in order to read the level of liquid butadiene. By slightly continuing to heat the vessel (3) and introducing liquid nitrogen in the Dewar vessel (2) attached to the reactor (4), the butadiene started to evaporate and moved to the reactor. This process was also favoured by introducing the bottom of the reactor in a Dewar vessel filled with liquid nitrogen. This ensures that all the evaporated butadiene is condensed inside the reactor. The heating of vessel (3) was stopped when the desired volume of butadiene was transferred into the reactor. All these operations took place in a completely welded installation (Fig. 1) and the way of butadiene moving is regulated through the vacuum cocks (1).

The isoprene (purchased from Merck) was freshly distilled onto TIBA prior to every polymerization, dosed in phials sealed with a flame and at the appropriate time introduced into the reactor.

The methanol (supplied by Fluka) was used as received.

3.2. Polymerization

Polymerization reactions were carried out according to the method described in detail in our previous papers [9, 10]. In brief, a glass, tube-like reactor of $100\,cm^3$ was evacuated to 10^{-1} mm Hg and then purged with dry argon. This process was repeated twice and then the reactor evacuated to 10^{-3} mm Hg. At this point the appropriate quantities of solvent (*n*-hexane) and the monomer were run into the reactor and magnetically stirred. In the case of butadiene polymerization, the reactor is welded on the installation for monomer dosing (Fig. 1), and after the monomer is passed into the reactor, the last is detached with a flame from the installation and further sealed with a flame.

Spherical phials, which contained the components of the catalyst system ($NdCl_3 \cdot 3TBP$ complex and TIBA) were situated in a side arm to the reactor, were broken with the stirrer contained within the reactor and their contents immediately mixed with the monomer/*n*-hexane solution. For a test of isoprene polymerization in standard conditions ([Isoprene] = 3 mol/l, $[Nd] = 4 \times 10^{-6}$ mol/g isoprene, [Al]/[Nd] = 30/1, polymerization temperature = 30°C), the volumes of the used solvent and reactants were: $17.5\,cm^3$ *n*-hexane, $7.5\,cm^3$ isoprene, $1\,cm^3$ of $NdCl_3 \cdot 3TBP$ complex solution and $1\,cm^3$ of TIBA solution.

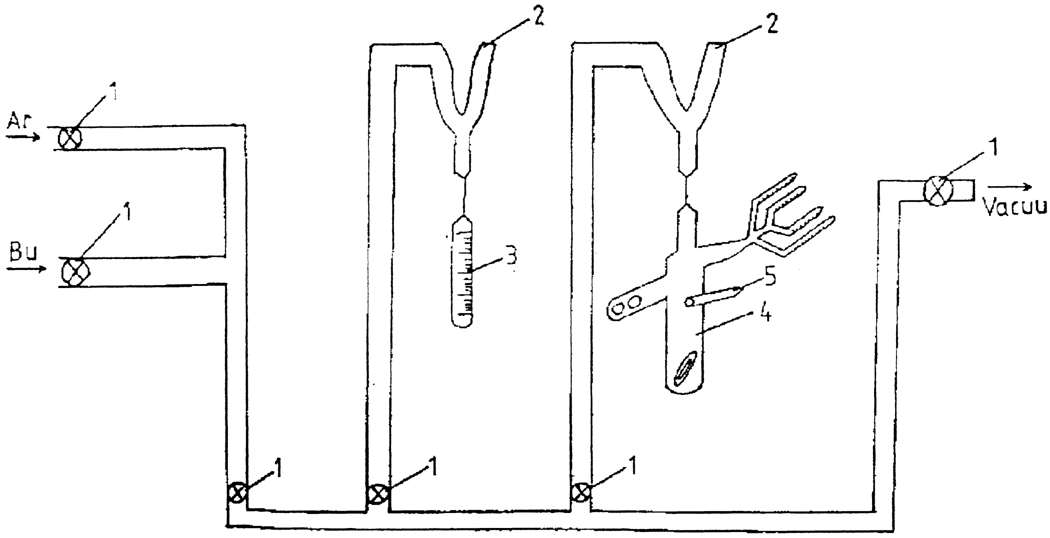


Fig. 1. Installation for butadiene dosing and polymerization with the $NdCl_3 \cdot 3TBP$–TIBA catalyst system: (1) vacuum cocks; (2) Dewar vessels; (3) vessel for butadiene dosing; (4) reactor; (5) inlet for solvent feed.

The isolated reactor was turned up, thus the whole mixture was passed into eight polymerization phials made from burettes, which were then alternatively sealed with a flame. During all this operation, the phials were kept in a Dewar vessel filled with liquid nitrogen in order to increase the passing rate and also to prevent the evaporation of butadiene, which may affect the sealing step. The frozen phials were quickly introduced in a thermostat bath at 30°C. After they reached this temperature, the level of the solution in each phial was marked on the glass wall of the phial. Following careful removal of the top of each polymerization phial by cutting them with a special knife at different polymerization times, the polymer so obtained was precipitated adding methanol containing butylated hydroxyl toluene to the contents of the phial. The precipitated polymer/solvent/monomer/catalyst residue mixture was filtered and the solid polymer was dried in an oven. The liquid was totally evaporated and the obtained solid residue was analysed. Neither polymer, nor oligomers were found, which is a proof for the completeness of the precipitation in methanol. Depending on the polymerization time, the quantity of the polymer obtained from one polymerization phial, as a result of a standard test, is from 0.0211 to 0.3551 g. The empty phials were then filled with distilled water up to the marked level in order to determine the initial volume of the polymerization mixture in each phial and thus to calculate the initial quantity of the monomer in each phial and the corresponding conversions.

4. Results and Discussion

For both isoprene and butadiene polymerization processes, the errors between the experimental concentration of the monomer and that calculated from the mathematical models applied were obtained. The accuracy of the calculated values is very high due to the generalized functions used, which eliminate the possible numerical errors in calculating the derivatives. The accuracy of the experimental data is influenced by the precision in marking the initial level of the polymerization mixture in each of the phial. For the same conditions, three polymerization experiments were performed in order to test reproducibility. The differences obtained for the experimental data are only at the third and at the fourth significant figure.

4.1. Isoprene

For both models analysed, the results concerning the isoprene polymerization process are listed in Table 2. One may observe that in the case of the monomolecular termination model systematically higher errors (E_a values from Table 2) are obtained than the errors calculated from the model considering the total absence of the termination reactions (E_b values from Table 2). Also using the monomolecular termination model, the value of the rate constant k_1 is variable from set 1 to set 6 of experiments and is negative when the generalized function from Eq. (29) was used. Therefore the polymerization model based on the total absence of

Table 2
The experimental and calculated data from the monomolecular termination model (N_a) and from the model considering the total absence of termination reactions (N_b) for the isoprene polymerization process with $NdCl_3 \cdot 3TBP$–TIBA catalyst system. The corresponding errors are denoted as E_a and E_b respectively*

No. of experiment	Polymerisation time (h)	N_{exp}	N_a	N_b	E_a (%)	E_b (%)
1	0.16	0.98	0.97	0.98	1.02	0
	0.33	0.96	0.95	0.96	1.04	0
	0.5	0.94	0.91	0.94	3.19	0
	1	0.89	0.87	0.89	2.25	0
	1.5	0.83	0.81	0.84	2.40	−1.20
	2	0.80	0.78	0.79	2.50	1.25
	3	0.71	0.73	0.71	−2.81	0
	4	0.63	0.65	0.63	−3.17	0
2	0.16	0.96	0.91	0.95	5.20	1.04
	0.33	0.92	0.90	0.90	2.17	2.17
	0.5	0.86	0.88	0.86	−2.32	0
	1	0.75	0.77	0.75	−2.66	0
	1.5	0.62	0.68	0.65	−9.67	−4.83
	2	0.56	0.55	0.56	1.78	0
	3	0.42	0.45	0.42	−7.14	0
	4	0.31	0.33	0.31	−6.45	0
3	0.16	0.93	0.90	0.92	3.22	1.07
	0.33	0.88	0.81	0.84	7.95	4.54
	0.5	0.81	0.73	0.78	9.87	3.70
	1	0.65	0.57	0.61	12/30	6.15
	1.5	0.48	0.44	0.47	8.33	0
	2	0.39	0.35	0.37	10.25	5.12
	3	0.21	0.25	0.22	−19.04	−4.76
	4	0.13	0.17	0.14	−30.76	−7.69
4	0.16	0.92	0.87	0.89	5.43	3.26
	0.33	0.85	0.79	0.80	7.05	5.88
	0.5	0.78	0.72	0.72	7.69	7.69
	1	0.56	0.50	0.51	10.71	7.14
	1.5	0.37	0.38	0.37	−2.70	0
	2	0.26	0.29	0.27	−11.53	−3.84
	3	0.12	0.17	0.14	−41.66	−16.66
	4	0.07	0.06	0.07	14.28	0
5	0.16	0.91	0.86	0.88	5.49	3.29
	0.33	0.80	0.74	0.77	7.50	3.75
	0.5	0.73	0.63	0.63	13.69	13.69
	1	0.45	0.49	0.46	−9.88	−2.22
	1.5	0.25	0.34	0.31	−36.0	−24.0
	2	0.18	0.25	0.21	−38.88	−16.66
	3	0.09	0.13	0.10	−44.44	−11.11
	4	0.05	0.03	0.04	40.0	20.0
6	0.16	0.98	0.94	0.97	4.08	1.02
	0.33	0.94	0.91	0.94	3.19	0
	0.5	0.89	0.88	0.91	1.12	−2.24
	1	0.82	0.85	0.83	−3.65	−1.21
	1.5	0.75	0.78	0.76	−4.0	−1.33
	2	0.70	0.72	0.70	−2.85	0
	3	0.59	0.61	0.59	−3.38	0
	4	0.50	0.52	0.49	−4.0	2.0

* $N = [M]/[M_0]$; $E = (N_{experimental} - N_{calculated})/N_{experimental} \times 100$.

the termination reactions is the most accurate for describing the isoprene polymerization process with $NdCl_3 \cdot 3TBP$–TIBA catalyst system. The product ($k_c \times C_0$) varies from set 1 to set 6 of experiments, the dependence of this product against [Al]/[Nd] molar ratio being plotted in Fig. 2.

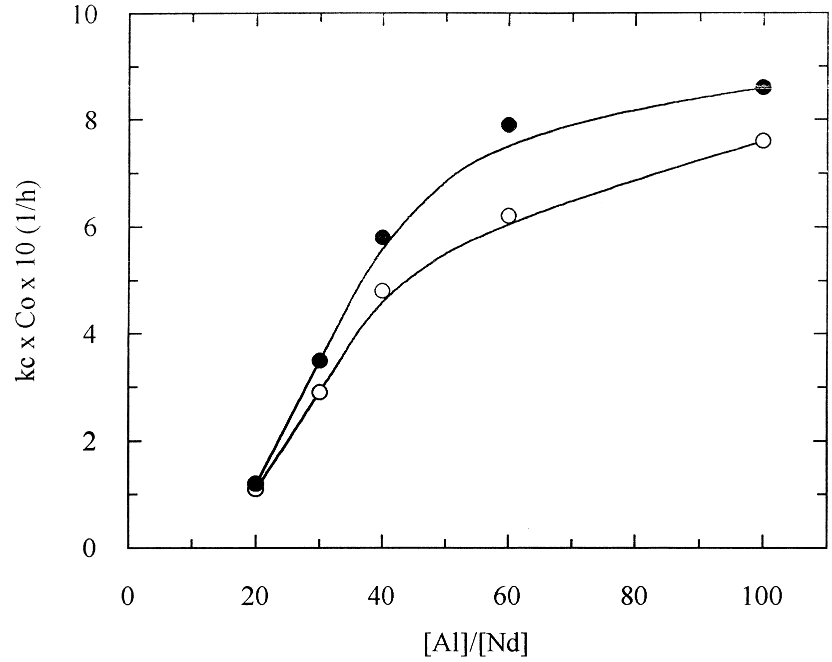


Fig. 2. The dependence of ($k_c \times C_o$) values against the [Al]/[Nd] molar ratio for the polymerization process of isoprene (○) and butadiene (●) with the $NdCl_3 \cdot 3TBP$–TIBA catalyst system (all the polymerization conditions were identical for both monomers).

4.2. Butadiene

Similar with isoprene polymerization, high errors (E_a values from Table 3) are obtained for monomolecular termination model and also negative k_1 values were calculated. Again, the best correlation with the experimental data was obtained for using the polymerization model considering the total absence of termination reactions (Table 3). The dependence of ($k_c \times C_0$) product against the [Al]/[Nd] molar ratio is presented in Fig. 2 (the ($k_c \times C_0$) values were calculated from Eq. (39)).

One may noticed that the ($k_c \times C_0$) product is always higher for butadiene than for isoprene, the difference increasing for higher [Al]/[Nd] molar ratios. This feature may be explained by the higher value of the k_c rate constant for butadiene than for isoprene (the catalyst system used was the same for both monomers).

From Fig. 2 it is also observed the significant increasing of the ($k_c \times C_0$) product with the increasing of the [Al]/[Nd] molar ratio up to 60–70. Besides, this fact is a strong argument for participation of the organoaluminium compound to the formation of the active centre either by alkyllation of the "*f*" transition metal [11] (according to the reaction (1)) or by formation of bridge complexes as shown in Fig. 3. However, this effect is present even for [Al]/[Nd] molar ratios in high stoichiometric excess, which indicates that additional roles may be played by the triisobutylaluminum, such as impurity scavenging.

5. Conclusions

The most appropriate model which describes the kinetic of the isoprene and butadiene polymerization reaction with the $NdCl_3 \cdot 3TBP$–TIBA catalyst system is the one considering no termination reactions during the polymerization process, which implies a constant active centres concentration. This does not exclude the possibility of transfer reactions with monomer or organoaluminum compound to occur. On the other hand, by using a monomolecular termination model we obtained high deviations from the experimental data, which means that the termination reactions are excluded.

The product between the propagation rate and the active centres concentration, obtained by solving the equations from the polymerization model in the absence of the termination reactions, depends significantly on the initial molar ratio used between the aluminium compound and the neodymium halide, which is an important argument for the participation of aluminium to the formation of the active centres and thus influences the stability and the reactivity of these centres during the polymerization process.

Table 3
The experimental and calculated data from the monomolecular termination model (N_a) and from the model considering the total absence of termination reactions (N_b) for the butadiene polymerization process with $NdCl_3 \cdot 3TBP$–TIBA catalyst system. The corresponding errors are denoted as E_a and E_b respectively*

No. of experiment	Polymerisation time (h)	N_{exp}	N_a	N_b	E_a (%)	E_b (%)
1	0.16	0.98	0.97	0.98	1.02	0
	0.33	0.96	0.95	0.96	1.04	0
	0.5	0.95	0.94	0.94	1.05	1.05
	1	0.89	0.87	0.88	2.25	1.12
	1.5	0.83	0.82	0.83	1.20	0
	2	0.79	0.76	0.78	3.79	1.26
	3	0.71	0.66	0.69	7.04	2.80
	4	0.64	0.57	0.61	10.93	4.68
2	0.16	0.95	0.90	0.94	5.26	1.05
	0.33	0.90	0.87	0.89	3.33	1.11
	0.5	0.86	0.84	0.84	2.32	0
	1	0.71	0.72	0.71	−1.40	0
	1.5	0.60	0.63	0.60	−5.0	0
	2	0.36	0.40	0.36	−5.88	1.96
	3	0.36	0.40	0.36	−11.11	0
	4	0.25	0.29	0.25	−16.0	0
3	0.16	0.91	0.86	0.90	5.49	1.09
	0.33	0.81	0.79	0.82	2.46	−1.23
	0.5	0.76	0.73	0.74	3.94	2.63
	1	0.52	0.56	0.55	−7.69	−5.76
	1.5	0.43	0.39	0.41	9.3	4.65
	2	0.32	0.28	0.30	12.5	6.25
	3	0.18	0.15	0.17	16.66	5.55
	4	0.10	0.08	0.09	20.0	10.0
4	0.16	0.88	0.85	0.87	3.40	1.13
	0.33	0.77	0.74	0.76	3.89	1.29
	0.5	0.66	0.63	0.67	4.54	−1.51
	1	0.45	0.48	0.44	−6.66	2.22
	1.5	0.31	0.34	0.30	−9.67	3.22
	2	0.22	0.19	0.20	13.63	9.09
	3	0.11	0.07	0.09	36.36	18.18
	4	0.05	0.03	0.04	40.0	20.0
5	0.16	0.88	0.82	0.86	6.81	2.27
	0.33	0.76	0.73	0.75	3.94	1.31
	0.5	0.64	0.62	0.65	3.12	−1.56
	1	0.44	0.47	0.43	−6.81	2.27
	1.5	0.29	0.32	0.28	−10.34	3.44
	2	0.19	0.18	0.18	5.26	5.26
	3	0.08	0.06	0.08	25.0	0
	4	0.04	0.01	0.03	75.0	25.0
6	0.16	0.97	0.95	0.96	2.06	1.03
	0.33	0.93	0.93	0.94	1.06	0
	0.5	0.91	0.90	0.91	1.09	0
	1	0.84	0.82	0.83	2.38	1.19
	1.5	0.76	0.73	0.75	3.94	1.31
	2	0.70	0.68	0.69	2.85	1.42
	3	0.56	0.54	0.57	3.57	−1.78
	4	0.47	0.46	0.47	2.12	0

* $N = [M]/[M_0]$; $E = (N_{\text{experimental}} - N_{\text{calculated}})/N_{\text{experimental}} \times 100$.

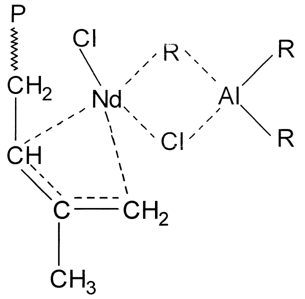


Fig. 3. The structure of the active centres including a bridge complex between the transition metal and the aluminium compound for the isoprene polymerization process with the $NdCl_3{\cdot}3TBP$–TIBA catalyst system.

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