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Optimization of the 1,3-Butadiene Cyclotrimerization Process by the Catalytic System $Et_3al_2cl_3/Ticl_4$: The Influence of the Parameters on the Selectivity of 1,5,9-Cyclododecatriene Formation

G. Lewandowski · M. Bartkowiak · E. Milchert

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Abstract The results of studies on the cyclotrimerization process of 1,3-butadiene to 1,5,9-cyclododecatriene in the $Et_3Al_2Cl_3/TiCl_4$ catalytic system in the toluene medium have been presented. On the basis of preliminary experiments of this process it was found that the molar ratio of $Et_3Al_2Cl_3$:Ti (X_1) in the range of 2–20, the $TiCl_4$ concentration (X_2) in the range of 2–20 mmol/dm^3, and temperature (X_3) in the range 40–80 °C have a significant influence on the 1,5,9-cyclododecatriene synthesis. In order to achieve the complete description of process, the statistical experimental design methods were utilized because they allows to obtain the mathematical model combining the characteristic magnitudes of process in the form of functional relationship. As a response function (objective function) was selected the selectivity of transformation to 1,5,9-cyclododecatriene in relation to consumed 1,3-butadiene ($S_{CDT/BD}$). It was found that the largest influence on the value of $S_{CDT/BD}$ has the molar ratio of $Et_3Al_2Cl_3$:Ti and temperature. Over the studied range of variation of independent factors, an increase in the $Et_3Al_2Cl_3$:Ti molar ratio, the $TiCl_4$ concentration, and temperature causes initially the increase of $S_{CDT/BD}$ to the maximum value, and subsequently its decline. The maximal selectivity of 1,5,9-cyclododecatriene formation ($S_{CDT/BD\ MAX} = 100$ mol%) was achieved at the molar ratio of EASC:Ti $X_1 = 14.8$, the $TiCl_4$ concentration $X_2 = 12.7$ mmol/dm^3, and at a temperature $X_3 = 54.6$ °C.

G. Lewandowski (✉) · M. Bartkowiak · E. Milchert
Institute of Organic Chemical Technology, Szczecin University of Technology, ul. Pułaskiego 10, 70-322 Szczecin, Poland
e-mail: grzegorz.lewandowski@ps.pl

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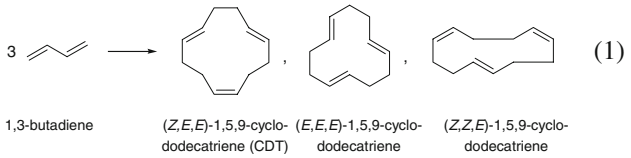
1 Introduction

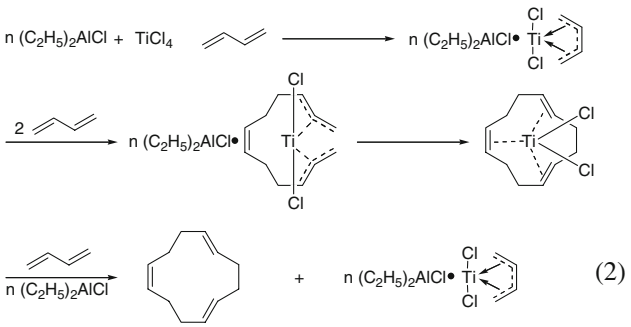
Polyamides (PA)—the products of polycondensation of diamines with dicarboxylic acids or the polymerization of lactams—belong to the most common and the most frequently utilized polymers [1]. Among many different kinds of polyamides, the industrial application have only found PA 6 (poly-ε-caprolactam), PA 11 (poly-ω-undecalactam, and PA 12 (poly-ω-dodecalactam) [2]. With regard to its properties, the PA 12 is one of the most interesting polyamides [3]. It contains a significantly smaller amount of the residual monomer, moreover, this polymer absorbs humidity from the environment in a lesser degree, while maintaining a higher flexibility even at a very low temperature (−70 °C). This causes that PA 12 is very often utilized as a high-quality design plastic [4, 5], particularly for the application under variable conditions of environment humidity or those required an enhanced mechanical, thermal, and electrical resistance, among others, for the manufacture of protective coatings of cables, conduits and pipes [6, 7], pipelines in the aerodynamic breaks [8], and automotive fuel system [9]. The raw material in the majority of known methods of PA 12 production is 1,5,9-cyclododecatriene [10–12] prepared as a result of cyclotrimerization of 1,3-butadiene (BD). The BD cyclotrimerization process is performed in presence of various catalytic systems comprised transition metal compounds: Ti, Cr, Ni, Mn and organic compound of aluminium. Detailed descriptions of the catalytic systems used for cyclotrimerization of BD were presented elsewhere [13, 14]. As a result from these studies

the highest activities in the BD cyclotrimerization process demonstrate $Et_2AlCl/TiCl_4$ and $Et_3Al_2Cl_3/TiCl_4$ catalytic systems. In the presence of these systems can be obtained three stereoisomers of 1,5,9-cyclododecatriene: (*Z*,*E*,*E*)-1,5,9-cyclododecatriene (CDT) (*Z*,*Z*,*E*)-1,5,9-cyclododecatriene, and (*E*,*E*,*E*)-1,5,9-cyclododecatriene [15, 16].



(1)

Quantitative ratios of these isomers depend on character of transition metal, type of ligands, and parameters of reaction [17]. The mechanism of the BD cyclotrimerization in presence of $TiCl_4$ as well as $C_6H_6 \cdot TiCl_2 \cdot Al_2Cl_6$ [18, 19] is the following:



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In this work has been presented the experimental results of the cyclotrimerization process BD to CDT in the $Et_3Al_2Cl_3/TiCl_4$ catalytic system in the toluene medium.

2 Experimental

2.1 Reagents

The BD cyclotrimerization in the $Et_3Al_2Cl_3/TiCl_4$ catalytic system was performed with the following reagents: toluene anhydrous, 99.8%, $Et_3Al_2Cl_3$ 25% in toluene, $TiCl_4$ 1 M in toluene, 1,3-butadien 99%, (*Z*,*E*,*E*)-1,5,9-cyclododecatriene, 98%, dodecane (standard), all of them from Aldrich, acetone from POCh Gliwice, Poland, and argon from Messer, Poland.

2.2 Apparatus

The BD cyclotrimerization was carried out under atmospheric pressure in the apparatus shown schematically in Fig. 1.

2.3 Procedure of Process Operation

With regard to an extreme sensibility of the titanium catalytic system to the presence of oxygen and humidity, before each experiment the reactor was held at a temperature of 115 °C for 30 min, and then was purged with dried argon for 60 min in order to remove the air and humidity from the apparatus. Such as prepared reactor (1) equipped with thermometer (2), mechanical stirrer with controlled number of revolutions (3), reflux condenser (4) and a bubbler made of Teflon for the introduction of BD was charged with fixed volume of toluene as a solvent, an appropriate aluminoorganic compound $Et_3Al_2Cl_3$ (reducing agent) and the cyclotrimerization catalyst ($TiCl_4$). The reactor was submerged in the water bath (6) with determined temperature and the process, so-called ageing of

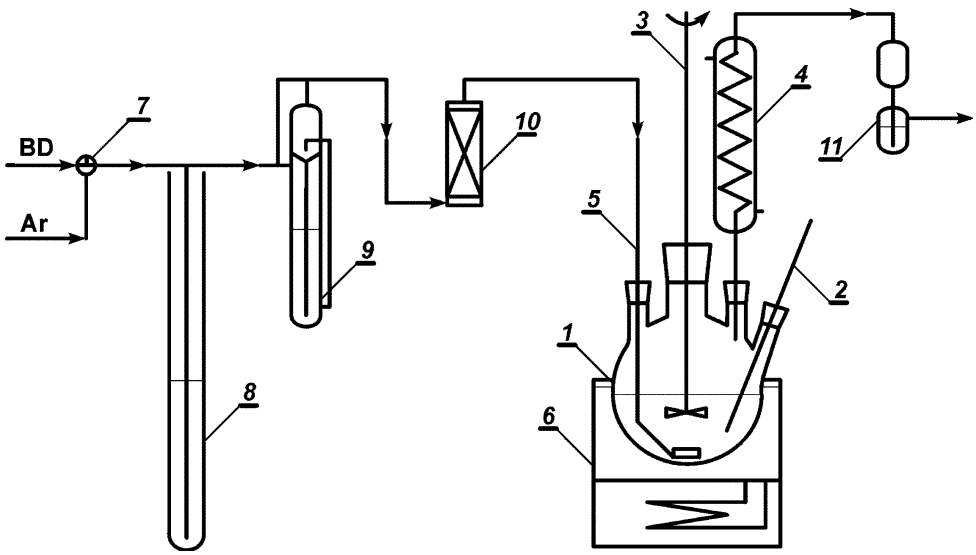


Fig. 1 Scheme of apparatus for cyclotrimerization of BD. 1, reactor; 2, thermometer; 3, mechanical stirrer; 4, reflux condenser; 5, BD bubbler; 6, water bath; 7, three-way valve; 8, hydraulic seal; 9, flowmeter; 10, adsorber of inhibitor of BD polymerization; 11, bubbles counter

catalyst, was carried out with a continuous feeding of argon for 20 min. The argon flow under overpressure reading on the hydraulic seal (8) protected the apparatus from the access of humidity and oxygen. After the ageing of catalyst the inflow of argon was closed by means of three-way valve and a BD was feeding. The flow rate of BD was controlled by means of graduated flowmeter (9) and adjust during synthesis so that to achieve a small flow of unreacted BD at the outlet of reflux condenser (4) which was controlled by the use of bubbler counter (11). Before feeding the reactor, the BD passed through the adsorber (10) in order to remove the polymerization inhibitor. The synthesis time was dependent on the amount of resulting cyclotrimerization products and amounted from 15 to 60 min. After that time the inflow of BD was closed by means of three-way valve and argon was again feeding for 20 min. Subsequently, a determined amount of acetone was added in order to deactivation of catalyst and the system was stirred for the next 20 min. The reaction product was cooled, weighted and analyzed by GC in order to determine the qualitative and quantitative composition of product. Based on the mass balance, for each synthesis was calculated the selectivity of transformation to CDT in relation to BD consumed ($S_{CDT/BD}$, mol%), as a quotient of number of moles of obtained CDT (n_{CDT}) and the number of moles of BD consumed (n_{BD}):

$$S_{CDT/BD} = \frac{n_{CDT}}{n_{BD}} \cdot 100 \quad (3)$$

2.4 Gas Chromatography

In order to determine the composition of products of BD cyclotrimerization process, the method of gas chromatography was used. Analyses were carried out on a Trace GC 2000 chromatograph (Thermo-Finnigan) equipped with computer system for data handling Chrom-Card for Trace GC. A DB-5 capillary column J&W Scientific 30 m × 0.25 mm × 0.25 μm was used. The detector temperature was 250 °C, whereas of sample chamber was 200 °C. The column temperature was programmed as follows: isothermally at 50 °C for 2.5 min, then increase to 250 °C at the rate 20 °C/min and isothermally at 250 °C for 2.5 min. The flow gas was as follows: air 250 cm^3/min, hydrogen 35 cm^3/min, carrier gas (helium) 0.7 cm^3/min.

The identification of components of post-reaction mixtures was performed by a comparison of the retention time of peaks on the chromatograms with the retention time of standard substances. An additional confirmation of peaks arrangement was achieved by the method of standard addition. A quantitative composition of postreaction mixtures was established by the method of internal standard. As the internal standard was used dodecane. The percentage content of determined component was calculated from the equation:

$$C_i = \frac{f_i \cdot A_i \cdot m_w}{A_w \cdot m_p} \cdot 100\%$$

where C_i, percentage concentration of component i (%), f_i, correction coefficient of determined component, A_i, the peak area of determined component, A_w, the peak area of the internal standard, m_w, mass of the internal standard added to mixture (g), m_p, mass of analyzed sample (g).

In all the calculations were not taken into account the losses resulting from a loss of reaction mass during taking samples for analyses.

2.5 Mathematical Description of the Process

Based on the preliminary investigations, it was fond that the temperature, the molar ratio of EASC:Ti, and $TiCl_4$ concentration have a significant influence on the result of BD cyclotrimerization. However, their influence is unambiguous and relatively difficult to the interpretation based on the result of random studies. In order to achieve a complete description of the essential process parameters on the results of BD cyclotrimerization; the statistical methods of experiments planning were used. These methods allow enhancing the effectiveness, and primarily, so-called "informativeness" of the experimental studies in relation to the traditional methods. A basis of statistical methods of experiments planning is the performance of studies according to a priori established plan of experiments, in which are predicted simultaneous changes of all significant parameters (independent factors) of the process. As a result of mathematical elaboration of result such performed experiments, with the application of methods of regression analysis is achieved so-called mathematical model of the process, combining the characteristic magnitudes of process in the form of functional dependences (regression equation) of the relationship approximating the experimental values of selected response function. A further statistical analysis enables the establishing of the significance of the coefficients and the final form and adequativeness toward the measurement results of obtained response function. This allows determining the function extremes—hence, its optimization.

The experimental studies of BD cyclotrimerization were performed according to rotatable-uniform design [20, 21]. This experimental design, in comparison with frequently used orthogonal design, is characterized by uniform inaccuracy, expressed by the constant variation of measurements inaccuracy. Each of the independent variables is here varied at five levels. This allows to obtain the regression equation in the form of polynomial of the second order.

Basis on the results of preliminary studies of BD cyclotrimerization and the analysis of literature reports it was found that the significant parameters influencing on the course of process are: the molar ratio of EASC:Ti, the $TiCl_4$ concentration, and temperature (Table 1).

As the response function characterizing the process of BD cyclotrimerization was assumed the selectivity of transformation to CDT in relation to BD consumed (Y). The studies were performed based on the design matrix of rotatable-uniform design (Table 2). The experimental value of response function was given in the last column.

Table 1 Independent factors and the ranges of their variations of the process of BD cyclotrimerization

Level	Coded value	Real value		
		Molar ratio EASC:Ti	$TiCl_4$ concentration (mmol/dm^3)	Temperature (°C)
	x_i	X_1	X_2	X_2
Basic	0	11.0	11.0	60.0
Higher	1	16.4	16.4	71.9
Lower	−1	5.7	5.7	48.1
Star higher	1.68	20.0	20.0	80.0
Star lower	−1.68	2.0	2.0	40.0

Table 2 Design matrix and experimental value of response function (Y)

Number of system	x_1	x_2	x_3	Y
1	−1	−1	−1	67.2
2	1	−1	−1	97.8
3	−1	1	−1	72.3
4	1	1	−1	94.5
5	−1	−1	1	27.0
6	1	−1	1	70.1
7	−1	1	1	53.9
8	1	1	1	92.2
9	−1.68	0	0	40.1
10	1.68	0	0	95.7
11	0	−1.68	0	72.2
12	0	1.68	0	96.2
13	0	0	−1.68	96.3
14	0	0	1.68	45.4
15	0	0	0	96.7
16	0	0	0	94.8
17	0	0	0	96.2
18	0	0	0	94.6
19	0	0	0	98.3
20	0	0	0	96.2

2.6 Statistical Analysis of Results

For the response function (Y) was determined a function approximating the measurement results, regression equation ($\hat{Y}$), in the form of polynomial of the second order [20, 21]:

$$\hat{Y}_i = b_o + \sum_{i=1}^{k} b_i x_i + \sum_{i<j}^{k} b_{ij} x_i x_j + \sum_{i=1}^{k} b_{ij} x_i^2 \tag{4}$$

where $\hat{Y}$, dependent variable, the response function Y, x_i, x_j, independent factors in the coded form ($i, j = 1,\ldots,k$), b_0, b_i, b_{ij}, b_{ii}, regression equation coefficient ($i, j = 1,\ldots,k$), k, the number of factors in the experimental design.

A transformation from the system of the independent factors in the natural form (real) to the coded form (dimensionless) was performed according to the normalization relationship:

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i} \tag{5}$$

where, x_i, coded value of variable in the point of the experimental design ($i = 1,\ldots,k$), X_i, natural value of variables in the point of the experimental design ($i = 1,\ldots,k$), X_{i0}, natural value of variables in the central point of the experimental design ($i = 1,\ldots,k$), ΔX_i, value of step along the x_i axis (natural).

The coefficients of the regression function ($\hat{Y}$), were calculated by the last-squares method. Subsequently, was calculated a variance of inaccurancy (S^2), which constitutes a measure of scattering of measurement result. This variance was determined taking into account the design systems, in which occur the repetitions of the input magnitude. In the rotatable-uniform design for $i = 3$ there are the systems comprising so-called design centre $u = 15$–20 (Table 2).

$$S^2 = \frac{1}{f_1} \cdot \sum_{i=1}^{n_0} \left(Y_i^0 - \hat{Y}_i^0\right)^2 \tag{6}$$

where S^2, variance of inaccuracy, Y_i^0, experimental value of the response function in the design centre ($i = 1,\ldots,n_0$), $\hat{Y}_i^0$, average value of the response function in the design centre ($i = 1,\ldots,n_0$) calculated by means of the regression equation, f_1, the number of degree of freedom of repeatability variance, $f_1 = n_0 - 1$, n_0, the number of experiment in the design centre.

In the successive stage was determined a variance of the adequacy (S_a^2), characterizing the scattering of the measurement results in relation to the values calculated from the regression equation.

$$S_a^2 = \frac{1}{f_2} \cdot \left[n_0 \left(\bar{Y}_i^0 - Y_i^0\right)^2 + \sum_{i=1}^{N-n} \left(Y_i - \hat{Y}_i\right)^2 \right] \tag{7}$$

where, S_a^2, variance of the adequacy, $\overline{Y_i^0}$, average experimental value of the response function in the design centre ($i = 1,\ldots,n_0$), Y_i, experimental value of the response function in the i-th experiment ($i = 1,\ldots,N - n_0$), $\hat{Y}_i$, value of the response function in the ith experiment calculated by means of the regression equation ($i = 1,\ldots,N - n_0$), f_2, the number of degree of freedom of variance of the adequacy: $f_2 = N - N_b - 1$, N, the total number of experiment in the experimental design: $N = 20$, N_b, the number of regression coefficients.

The above-mentioned measures of errors were supplemented by the coefficient of multidimensional correlation R:

$$R = \left[\frac{\sum_{u=1}^{n}\left(\hat{Y}^{(u)} - Y_s\right)^2}{\sum_{u=1}^{n}\left(Y^{(u)} - Y_s\right)^2}\right]^{\frac{1}{2}} \quad (8)$$

where, Y_s, average experimental value of the response function in the experimental design.

A statistical verification of significance of the regression equation coefficients was performed on the basis of the Student's t-test. In the subsequential stage of statistical analysis was calculated a value of the Fisher–Snedecor test ($F = S^2/S_a^2$). If $F < F(\alpha)$, a function is recognized as adequate. Both tests were carried out for the significance level $\alpha = 0.05$. The values of the coefficients of the regression function, values of variance of inaccuracy, variance of the adequacy, and the value of the Fisher–Snedecor test and its critical value were summarized in Table 3.

All the coefficients significantly influence on a value of the $\hat{Y}$ function for assumed level of significance $\alpha = 0.05$. As results from value of the F-test, the function $\hat{Y}$ adequately describes the experimental results. At the bottom of Table 4 was also given a value of the coefficient of multidimensional correlation $R(\alpha)$.

The optimization of the regression equation $\hat{Y}$ was performed numerically with application of the Hooke-Jeeves and Box methods [21]. Both methods gave almost identical optimal value of the independent variables (Table 4).

The influence of the particular independent variables on the value of the response function was analyzed on the basis of spatial and two-dimensional section of surfaces of responses plotted in Surfer 5.01 program. Sections represent the lines of the same value of responses function during the changes of a couple of independent variables from the minimum value to the maximum value. Under these conditions, the third factor was established at a level ensuring the function maximum. For this purpose the three charts were plotted, one chart per each couple of independent variables: x_1 i x_2, x_1 i x_3, x_2 i x_3.

Table 3 Coefficients of the regression equation and measures of errors

	Selectivity of transformation to CDT in relation to BD consumed (Y)		
	Coded	$\hat{Y_1}$	Natural
b_0	96.1654		−92.9708
b_1	16.6002		8.2644
b_2	6.6020		−0.2231
b_3	−12.6825		5.1019
b_{11}	−10.1915		−0.3559
b_{12}	−1.5250		−0.0532
b_{13}	3.4500		0.0542
b_{22}	−4.4287		−0.1546
b_{23}	5.7750		0.0907
b_{33}	−9.1486		−0.0647
S^2		1.83	
$S_a{}^2$		7.39	
f_1		5	
f_2		9	
F		4.04	
$F(\alpha)$		4.84	
Adequate function			
$R(\alpha)$		0.99	

2.7 The Influence of Process Parameters on the Selectivity of Transformation to CDT in Relation to BD Consumed (Y)

The analysis of the regression equation $\hat{Y}$ (Table 3) of the selectivity of transformation to CDT in relation to BD consumed indicates, that all the independent variables taken into account in the experimental design significantly influence on the function value. Over investigated range of variations of the independent factors, an increase in the

Table 4 Optimal parameters of the regression equation $\hat{Y}$

Response function	Maximum value		Optimum values of parameters					
	Experimental (Mol%)	Calculated (Mol%)	Molar ratio EASC:Ti (mmol/dm^3)		$TiCl_4$ concentration (mmol/dm^3)		Temperature (°C)	
			x_1	X_1	x_2	X_2	x_3	X_3
Y	100.0	109.2	0.715	14.8	0.324	12.7	−0.455	54.6

molar ratio of EASC:Ti, the $TiCl_4$ concentration, and temperature initially causes the increase in the selectivity of transformation to CDT to a maximum value and then its decrease. CDT with the maximum selectivity (100 mol%) is achieved at the molar ratio of EASC:Ti $X_1 = 14.8$, the $TiCl_4$ concentration $X_2 = 12.7$ mmol/dm^3, and at temperature $X_3 = 54.6$ °C.

An analysis of the course of isoline of the selectivity of transformation to CDT in relation to BD consumed as a function of the molar ratio of EASC:Ti and the $TiCl_4$ concentration reveals that the molar ratio of EASC:Ti has considerably larger influence on the function value than that of the $TiCl_4$ concentration (Fig. 2). About this testifies a relatively large thickening of isolines of the selectivity as a function of the molar ratio of EASC:Ti, particularly in the range of 2–8 and almost a parallel course of these isolines in relation to the axis of the $TiCl_4$ concentration. One can come to the same conclusions analysing the $\hat{Y}$ regression equation (Table 3). The values of the coefficients of square terms for the EASC:Ti molar ratio and the $TiCl_4$ concentration have a negative value and they not too differ to each other ($b_{11} = -0.3559$, $b_{22} = -0.1546$). Whereas the values of the coefficients of linear terms for the EASC:Ti molar ratio and the $TiCl_4$ concentration differ a great many. The linear coefficient $b_1 = 8.2644$, whereas the linear coefficients $b_2 = -0.2231$. This cause that a change of the molar ratio of EASC:Ti is considerably larger than a change of the selectivity caused by a change of selectivity caused by a change of the $TiCl_4$ concentration.

Such influence of EASC:Ti molar ratio and $TiCl_4$ concentration may result from a relatively large activity of EASC/$TiCl_4$ catalytic system. With such assumption, the system can forms the active complex catalyzing the selective cyclotrimerization of BD to CDT even at low concentration of $TiCl_4$ and appropriately high molar ratio of EASC:Ti. With the reverse assumption, that the catalytic system possesses a low or moderate activity, one should expect that the effectiveness and selectivity of transformation to CDT in relation to BD consumed will be growing along with the increase in the $TiCl_4$ concentration.

With the established at the most beneficial levels of the $TiCl_4$ concentration, $X_2 = 12.7$ mmol/dm^3 and temperature, $X_3 = 54.6$ °C, the selectivity of transformation to CDT in relation to BD consumed increases from 49 to 100 mol% along with increase in the of EASC:Ti molar ratio. However, the selectivity of transformation to CDT at a level above 95 mol% can be achieved over a relatively wide range of variations of both analysed parameters, in the area limited by isoline 95 mol%. Hence, at the optimal temperature $X_3 = 54.6$ °C and the molar ratio of EASC:Ti $X_1 = 14.8$, the synthesis of CDT can be carried out in the range of $TiCl_4$ concentration $X_2 = 4$–18 mmol/dm^3, while achieving the CDT selectivity above 95 mol%. When the temperature and $TiCl_4$ concentration are established at the optimal level, respectively, $X_1 = 12.7$ mmol/dm^3 and $X_3 = 54.6$ °C, the selectivity of transformation to CDT in relation to BD consumed at a level above 95 mol% can be achieved at the EASC:Ti molar ratio in the range $X_1 =$ 9–20.

The course of isoline of the selectivity of transformation to CDT in relation to BD consumed is slightly different with simultaneous variations of the EASC:Ti molar ratio and temperature (Fig. 3). Over the whole investigated range of the EASC:Ti molar ratio, an increase of temperature from minimal value $X_3 = 40$ °C to the maximum $X_3 = 80$ °C initially causes the increase and then a decrease in the selectivity of transformation to CDT in relation to BD consumed (at established optimal concentration of $TiCl_4$ $X_2 = 12.7$ mmol/dm^3). The highest CDT selectivity is achieved at temperature $X_3 = 54.6$ °C.

A relatively large effect of the interaction of the EASC:Ti molar ratio and temperature was observed.

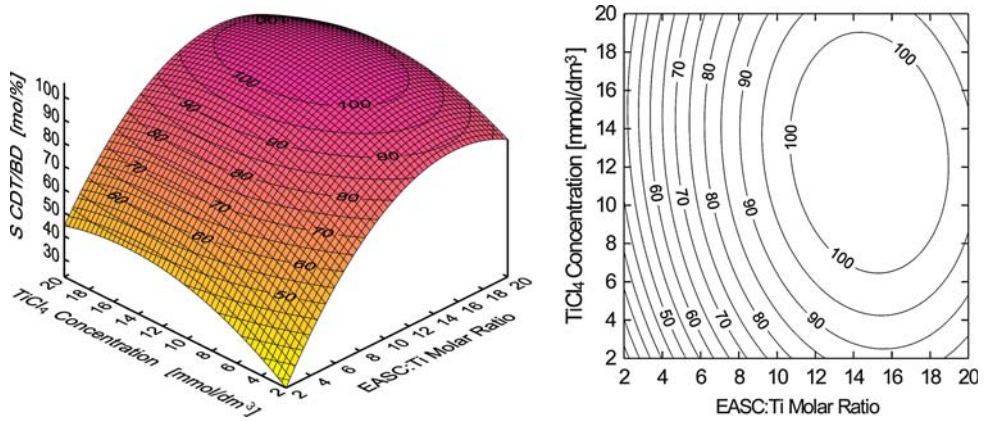


Fig. 2 Influence of EASC:Ti molar ratio and $TiCl_4$ concentration on the selectivity of transformation to CDT in relation to BD consumed; temperature 54.6 °C

A simultaneous the decrease of temperature from the maximum value $X_3 = 80$ °C to minimum value $X_3 = 40$ °C and the increase of the EASC:Ti molar ratio from the minimum value $X_1 = 2$ to maximum value $X_1 = 20$ causes the increase in the selectivity of transformation to CDT in relation to BD consumed considerably larger than a decrease and increase, respectively, a temperature and the EASC:Ti molar ratio at the established at the optimal levels of remaining two parameters. An analysis of the $\hat{Y}_1$ regression equation (Table 3) reveals, that the values of coefficients responsible for the square effects of the EASC:Ti molar ratio and temperature are almost identical (in coded scale). The values of coefficients responsible for the linear effects of the EASC:Ti molar ratio and temperature (in coded scale) differ rather significantly and they have opposite signs. This causes, as can be observed in Fig. 3, that a considerably larger increase in the selectivity of transformation to CDT in relation to BD is caused by an increase of the EASC:Ti molar ratio from the minimum value $X_1 = 2$ to optimum value $X_2 = 14.8$, than be lowering of temperature from the maximum value $X_3 = 80$ °C to optimal value $X_3 = 54.6$ °C (at the established most beneficial concentration of $TiCl_4$ $X_2 = 12.7$ mmol/dm^3). However, from the technological point of view, a larger attention should be given to maintain the established molar ratio of EASC:Ti than to strict comply with temperature regime.

The course of isoline of the selectivity of transformation to CDT in relation to BD consumed as a function of the $TiCl_4$ concentration and temperature (Fig. 4) confirms a relatively small influence of the $TiCl_4$ concentration, that was previously observed for the course of the selectivity of transformation to CDT in relation to BD consumed during the changes of the EASC:Ti molar ratio and the $TiCl_4$ concentration (Fig. 2). This is testified by a larger curving of isoline than previously, and is associated with the occurrence of greater interaction of the $TiCl_4$ concentration and temperature. This is confirmed by the value of the b_{23} coefficient in the $\hat{Y}_1$ regression equation (Table 3), which in the coded scale is almost . fold larger than the value of the b_{12}.

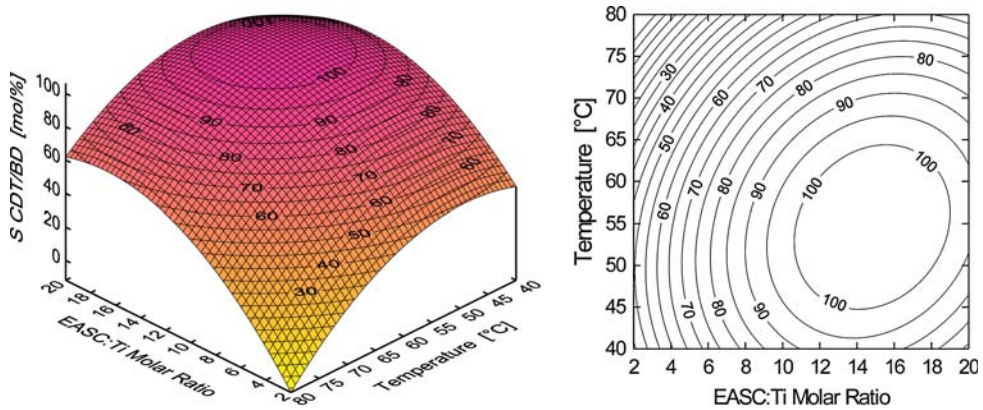


Fig. 3 Influence of the EASC:Ti molar ratio and temperature on the selectivity of transformation to CDT in relation to BD consumed; $TiCl_4$ concentration 12.7 mmol/dm^3

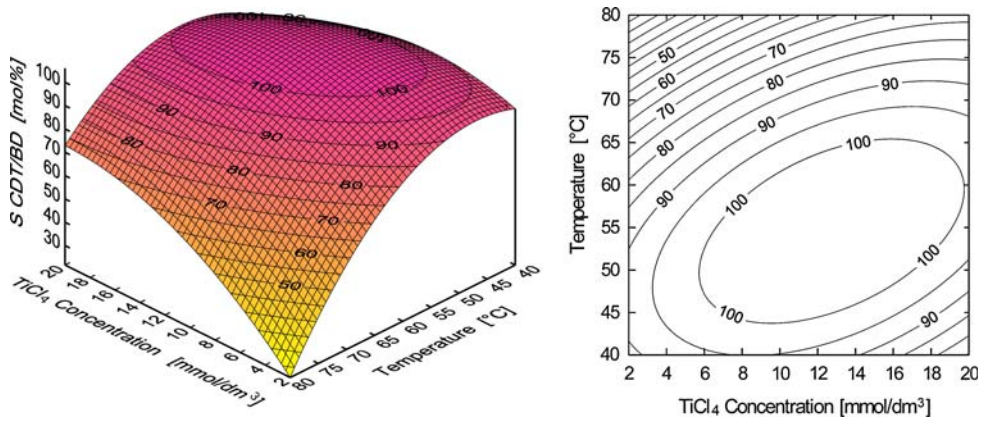
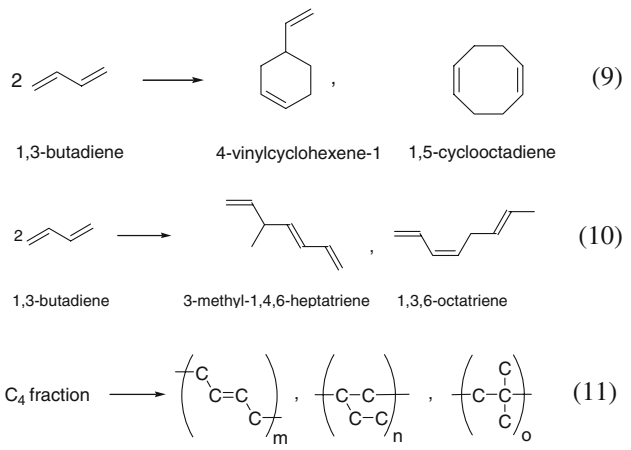


Fig. 4 Influence of the $TiCl_4$ concentration and temperature on the selectivity of transformation to CDT in relation to BD consumed; EASC:Ti molar ratio 14.8

An analysis of the course of the selectivity of transformation to CDT in relation to BD consumed as a function of the $TiCl_4$ concentration and temperature (Fig. 4), suggest that the CDT is obtained with a high selectivity over a relatively wide range of variations of both parameters.

The area limited by isoline of selectivity 95 mol% covers almost the whole investigated range of variations of the $TiCl_4$ concentration and a larger part of investigated temperature interval, however, with some limitations. The high selectivity of transformation to CDT in relation to BD consumed is achieved at low concentrations of $TiCl_4$ ($X_2 = 4$ mmol/dm^3), but the temperature also have to be a relatively low $X_3 < 50$ °C. At the $TiCl_4$ concentration in the range $X_2 = 4$–10 mmol/dm^3, the CDT synthesis can be carried out at adequately higher temperature (50–60 °C). Above the $TiCl_4$ concentration $X_2 > 10$ mmol/dm^3, the range of temperature possible for the application becomes limited also from the bottom. At these concentrations of $TiCl_4$, the process temperature should not exceed 65 °C and it cannot be lower than 50 °C.

It should be underlined that for the $TiCl_4$ concentration $X_2 = 2$ mmol/dm^3 at temperature close to $X_3 = 80$ °C, the catalytic system EASC/$TiCl_4$ completely losses the activity in the selective conversion of BD to CDT. A similar effect can be caused by lowering the molar ratio of EASC:Ti to $X_1 = 2$ and $TiCl_4$ concentration to $X_2 = 2$ mmol/dm^3 or by lowering the molar ratio of EASC:Ti to $X_1 = 2$ and by elevation of temperature to $X_3 = 80$ °C. In these conditions significant increases of selectivities of BD transformation to cyclo- and lineardimers and polymers were observed [17].



3 Conclusions

In the investigated ranges of variations of parameters of the BD cyclotrimerization process over the $Et_3Al_2Cl_3/TiCl_4$ catalytic system in the toluene medium: the molar ratio of $Et_3Al_2Cl_3$:Ti (X_1) within the range of 2–20, the $TiCl_4$ concentration (X_2) in the range of 2–20 mmol/dm^3, and the temperature (X_3) over the range 40–80 °C, can be obtained CDT with a very high selectivity. A complete description of the process were achieved by the utilize of the statistical method of the experimental design, which allow to obtain the mathematical model relating the selectivity of transformation of BD to CDT ($S_{CDT/BD}$) and above mentioned magnitudes being characteristic for the process in the form of the functional relationship. The optimization of the function, which allow to obtain the parameters of the maximum selectivity of transformation of BD to CDT ($S_{CDT/BD\ MAX} = 100$ mol%): molar ratio of $Et_3Al_2Cl_3$:Ti $X_1 = 14.8$, concentration of $TiCl_4$ $X_2 = 12.7$ mmol/dm^3, and the temperature $X_3 = 54.6$ °C. An increase or decreases in the molar ratio of $Et_3Al_2Cl_3$:Ti, the $TiCl_4$ concentration and temperature in relation to the optimal parameter causes the decrease in $S_{CDT/BD}$.

It was found that under extremely unfavourable conditions of BD cyclotrimerization (low molar ratio of EASC:Ti, low $TiCl_4$ concentration, and high temperature) the selectivity of transformation to the dimmers or/and polymers is essentially increased. Most probably, it was caused by insufficient amount of $TiCl_4$ necessary for the formation of the active catalytic complex. Other reason can be a decrease in the activity of catalytic complex under the influence of high temperature or the formation of other catalytic forms which do not exhibit the activity in the selective conversion of BD to CDT. Further studies should be undertaken to explore this issue.

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