

Obtaining Poly (dimethylsiloxane)- α , ω - Diols Using the Heterogeneous Catalysis: The Optimization of the Reaction Conditions

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ABSTRACT

Cationic heterogeneous polymerization of a mixture of dimethylcyclosiloxanes is studied, with the aim to evaluate the influence of different factors (temperature, reaction time, the amount of catalyst and water) on the monomers' conversion and on the molecular weight of the obtained polymer.

A second order, central, composite, rotatable design is used in order to carry out the experiments.

The experimental results are processed on a PC-AT computer in order to obtain the regression equations or the response surfaces for the studied properties. This program allows the study of the possibilities of the process optimization.

Key Words

cyclosiloxanes, cationic polymerization, experimental design, molecular weight, regression equations.

INTRODUCTION

References have mentioned some trials of computer-assisted modelling and experimental data processing for heterogeneous catalyzed polymerization of cyclosiloxanes. So, for polymerization of hexamethyldisiloxane with octamethylcyclotetrasiloxane (D_4) and the rearrangement of hexadecamethylheptasiloxane or

of docosamethylheptasiloxane using sulphuric acid activated earth as catalyst, a four step mechanism was proposed in order to appreciate the way in which the equilibrium was reached [1]. The expressions for the reaction rates were reduced to a finite number of ordinary, nonlinear differential equations. They were solved using Runge-Kutta

numerical method of integration. The calculated distributions of molecular weights were in good agreement with experimental data.

Braun et al. [2], studied cationic polymerization of cyclosiloxanes compounds and used a computer-assisted simulation to verify the proposed mechanism using the previous model of Hamann [3].

For simulating chain-rings kinetic dependencies in octamethylcyclosiloxane cationic polymerization, the Monte-Carlo method was used [4].

In this work cationic heterogeneous polymerization of a mixture of dimethyl - cyclosiloxanes was studied to evaluate the influence of different factors (temperature, time, the amount of catalysts and water) on the monomer's conversion and the molecular weight of the obtained polymer.

EXPERIMENTAL

Materials

Materials as exactly reported in Ref [5].

Experiments were performed in a glass reactor equipped with a stirrer, control

thermometer and a back-flow condenser which communicates with atmosphere through a tube containing calcium chloride (CaCl_2). The calculated amounts of monomers (dried on CaCl_2 and distilled), catalyst (dried) and water were introduced into the reactor. The operating conditions were established according to the experimental design.

Experimental Design

In order to reduce the number of experiments and the amount of materials and energy, a second order, central, composite, rotatable design was used [6].

The independent variables were as follows:

- reaction temperature (x_1), °C;
 - reaction time (x_2), hours;
 - the amount of catalyst (x_3), % from the amount of monomer;
 - the amount of water (x_4), % from the amount of monomer;
- and as dependent variables, experimentally determined:
- monomers conversion (y_1);
 - the molecular weight of the obtained polymer (y_2).

Table 1. Coding of the independent variables

Variable	Coded values				
	-2	-1	0	1	2
Reaction temperature, (x_1), °C	30.00	50.00	70.00	90.00	100.00
Reaction time, (x_2), hours	0.25	0.75	1.25	1.75	2.25
Amount of catalyst, (x_3), % of the amount of monomer	0.50	2.00	3.50	5.00	6.50
Amount of water, (x_4), % of the amount of monomer	0.10	0.30	0.50	0.70	0.90

Table 2. Experimental design (coded and actual) and experimental data

Exp no.	Reaction temperature, °C		Reaction time, hours		Amount of catalyst, %		Amount of water, %		Conversion, %	Molecular weight
	Coded	Actual	Coded	Actual	Coded	Actual	Coded	Actual		
1	-1	50.0	-1	0.75	-1	2.0	-1	0.3	31.9	68630
2	+1	90.0	-1	0.75	-1	2.0	-1	0.3	84.1	61065
3	-1	50.0	+1	1.75	-1	2.0	-1	0.3	49.4	75984
4	+1	90.0	+1	1.75	-1	2.0	-1	0.3	93.2	74235
5	-1	50.0	-1	0.75	+1	5.0	-1	0.3	73.4	102151
6	+1	90.0	-1	0.75	+1	5.0	-1	0.3	92.2	85138
7	-1	50.0	+1	1.75	+1	5.0	-1	0.3	89.7	115753
8	+1	90.0	+1	1.75	+1	5.0	-1	0.3	96.0	100152
9	-1	50.0	-1	0.75	-1	2.0	+1	0.7	14.4	47156
10	+1	90.0	-1	0.75	-1	2.0	+1	0.7	79.1	57645
11	-1	50.0	+1	1.75	-1	2.0	+1	0.7	46.5	67033
12	+1	90.0	+1	1.75	-1	2.0	+1	0.7	87.2	62436
13	-1	50.0	-1	0.75	+1	5.0	+1	0.7	58.8	83796
14	+1	90.0	-1	0.75	+1	5.0	+1	0.7	89.9	72575
15	-1	50.0	+1	1.75	+1	5.0	+1	0.7	86.7	108188
16	+1	90.0	+1	1.75	+1	5.0	+1	0.7	94.5	89462
17	-2	30.0	0	1.25	0	3.5	0	0.5	34.1	96257
18	+2	110.0	0	1.25	0	3.5	0	0.5	90.2	62877
19	0	70.0	-2	0.25	0	3.5	0	0.5	49.4	70483
20	0	70.0	+2	2.25	0	3.5	0	0.5	91.5	86351
21	0	70.0	0	1.25	-2	0.5	0	0.5	86.6	31931
22	0	70.0	0	1.25	+2	6.5	0	0.5	92.6	135000
23	0	70.0	0	1.25	0	3.5	-2	0.1	90.8	105822
24	0	70.0	0	1.25	0	3.5	+2	0.9	80.0	68292
25	0	70.0	0	1.25	0	3.5	0	0.5	87.3	87856
26	0	70.0	0	1.25	0	3.5	0	0.5	87.5	87762
27	0	70.0	0	1.25	0	3.5	0	0.5	88.1	87592
28	0	70.0	0	1.25	0	3.5	0	0.5	87.1	87920
29	0	70.0	0	1.25	0	3.5	0	0.5	86.8	88321
30	0	70.0	0	1.25	0	3.5	0	0.5	86.5	89032
31	0	70.0	0	1.25	0	3.5	0	0.5	87.4	87830

The independent variables were coded according to the relation:

$$X_i = \frac{x_i - x_{i0}}{\Delta x_i} \quad (1)$$

where:

- x_i - dimensionless, coded variable;
- x_i - actual variable;
- x_{i0} - central value of actual variable;
- Δx_i - factorial increment of the variable.

In Table 1 the coding of variables are presented.

The experimental design (coded and actual) and the obtained experimental results are presented in Table 2.

The experiments were performed in a random order. For every experiment, conversion and molecular weights were determined. The conversion was determined by measuring the amount of unreacted dimethylcyclosiloxanes which was separated by distilling the final mixture. The

Table 3. Regression analysis

Type	Regression coefficients		Eigenvalues	
	Conversion	Molecular weight	Conversion	Molecular weight
a ₀	87.2143	38044.7140	0.69593	196.06772
a ₁	15.7333	-5530.9583	-1.08161	-584.05790
a ₂	8.4833	6100.9583	-4.17125	-3263.13190
a ₃	15.1417	18715.3750	-11.64907	-4034.75920
a ₄	3.1000	-7078.2083		
a ₁₁	-5.3015	-2567.6266		
a ₁₂	4.2625	960.1875		
a ₂₂	-3.2265	-2830.1266		
a ₁₃	8.5875	-3696.1875		
a ₂₃	-0.8875	1543.9375		
a ₃₃	8.1890	-1593.0016		
a ₁₄	1.1500	1117.0625		
a ₂₄	1.6250	1050.4375		
a ₃₄	0.6250	-220.5625		
a ₄₄	0.5110	-695.1266		

molecular weight of the polymer was determined by viscosimetric method. The results are presented in the last two columns of the Table 2.

DISCUSSION

It was assumed that the relationship between the dependent variables and the independent ones could be approximated by an equation of the following form:

$$y = a_0 + a^T x + x^T A x \quad (2)$$

where y is the dependent variable or a response surface, A is the regression coefficients matrix, x is the vector of the independent variables and a_0 is the intercept (T stands for the transpose vector).

For the determination of regression coefficients from equation (2) the multiple regression method was used. Experimental data were processed on a PC-AT computer, and regression equations were obtained for the two properties taken into account, their coefficients being presented in Table 3.

The program allowed the study of the possibilities of the process optimization and plotting of the constant level curves of the response surfaces in all the fields given by the consecutive combination of two independent

variables (the third and the fourth variable being taken at their central values). In Table 3 the eigenvalues of the two response surfaces determined by solving the equation are also given (equation 3).

$$\det (A - \lambda I) = 0 \quad (3)$$

In this equation λ is the vector of the eigenvalues and I the unity matrix.

As can be seen, for both properties taken into account, one eigenvalue is positive and the others are negative so that the response surfaces are undetermined, or in the form of a saddle in the space of the four independent variables. As we will see later, there are some optimum response surfaces for some combination of two independent variables [7].

The insignificant regression coefficients were rejected by means of the "t" test, and regression equations were tested against the "F" test.

In Figures 1 to 6 the constant level curves for conversion against two variables and at central values for the others are presented.

In Figure 1 constant level curves of conversion against reaction temperature and reaction time are presented. One may notice that the greater these variables are, the greater the conversion will be.

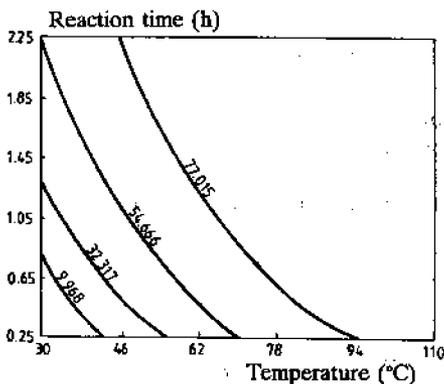


Fig.1. Constant level curves of conversion against reaction temperature (x_1) and reaction time (x_2) (the rest of variables are taken in the middle of their variation domain).

Stationary point, placed in the experimental domain, is a maxima and its coordinates are $x_{1s} = 96\text{ }^\circ\text{C}$ and $x_{2s} = 1.4775$ hours (the third variable x_3 , the amount of catalyst, and the fourth variable x_4 , the amount of water, are at their constant, central values). Figure 1 shows, also, that the greatest increase in conversion is obtained when both variables increase.

The constant level curves of conversion in the domain of the two variables $x_1 - x_3$ (the reaction temperature - the amount of catalyst) are given in Figure 2.

This figure shows an increase of conversion when the two variables increase and presents a maxima value for $x_1 = 95.6\text{ }^\circ\text{C}$ (very close to that in Figure 1) and $x_3 = 3.625\%$.

In Figure 3 the variables taken into account are x_1 (the reaction temperature) and x_4 (the amount of water). One may notice an increase in the value of conversion when the reaction temperature increases. The influence of the amount of water is smaller and almost insignificant (the curves are almost parallel to the x_4 axis). The stationary point, placed in the experimental domain, is a maxima value and its coordinates are $x_{1s} = 102\text{ }^\circ\text{C}$ and $x_{4s} = 0.65\%$.

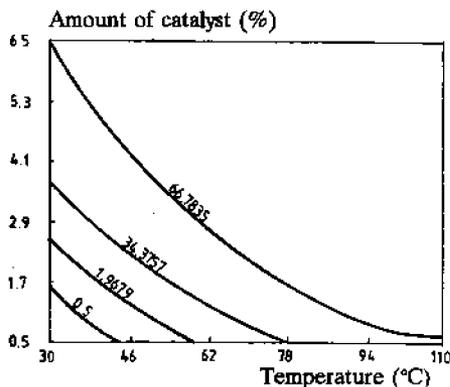


Fig.2. Constant level curves of conversion in the experimental field of the reaction temperature (x_1) and the amount of catalyst (x_3) (the rest of variables are taken in the middle of their variation domain).

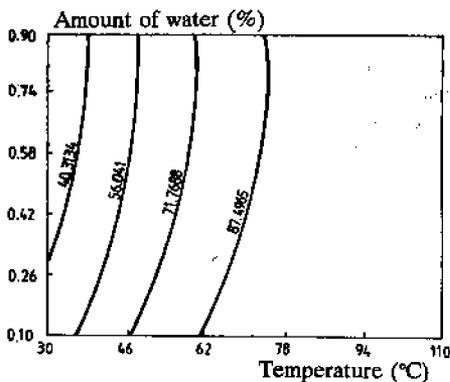


Fig.3. The influence of the reaction temperature (x_1) and the amount of water (x_4) on conversion (the rest of variables are taken in the middle of their variation domain).

The reaction time (x_2) and the amount of catalyst (x_3) are two variables with a strong influence on conversion. The constant level curves of conversion against these two variables are presented in Figure 4.

It is evident that conversion increases when

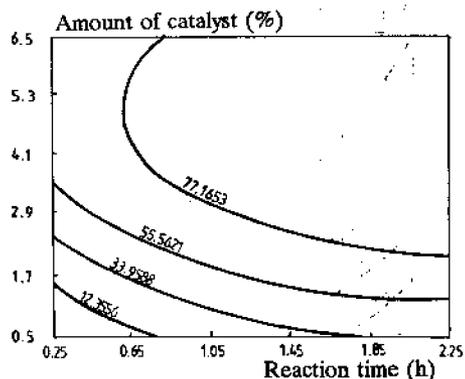


Fig.4. constant level curves of conversion in the experimental field of the reaction time (x_2) and the amount of catalyst (x_3) (the rest of variables are taken in the middle of their variation domain).

both variables increase, but the influence of the amount of catalyst is stronger. The stationary point is placed in the experimental domain, and it, too is a maxima, and its coordinates are $x_{25}=1.85$ hours and $x_{35}=4.79\%$.

In Figure 5, as in Figure 3, one may notice a small influence of the fourth variable (the amount of water) on the conversion.

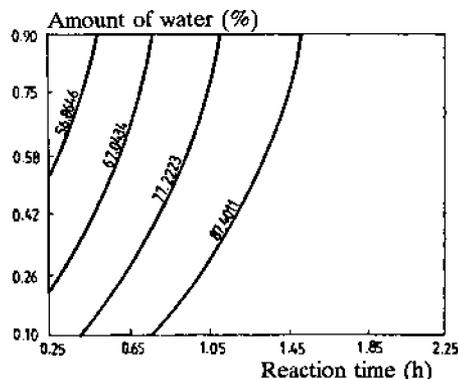


Fig.5. Constant level curves of conversion in the experimental field of the reaction time (x_2) and the amount of water (x_4) (the rest of variables are taken in the middle of their variation domain).

The greatest increase in conversion may be obtained when the reaction time increases. This figure has, also, a stationary point placed in the experimental domain, that is a maxima, and its coordinates are $x_{25}=1.99$ hours and $x_{45}=0.64\%$.

The insignificant influence of the amount of water on conversion is also pointed out in Figure 6.

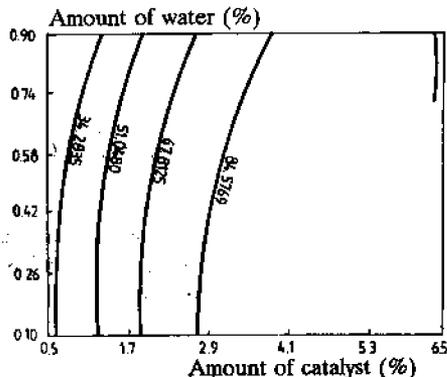


Fig.6. Curves of constant conversion yield in the experimental field of the amount of catalyst (x_3) and the amount of water (x_4) (the rest of the variables are taken in the middle of their variation domain).

The variables taken into account in this case are the amount of catalyst (x_3) and the amount of water (x_4). One may notice a considerable increase of conversion when the amount of catalyst increases.

Analyzing the figures presented above leads to the conclusion that the conversion is strongly influenced by the amount of catalyst, the reaction temperature and the reaction time. The amount of water has an insignificant influence on conversion.

In Figures 7 to 12 the constant level curves of the molecular weight of the obtained polymer against two variables and at central values for the others are presented.

In Figure 7 the simultaneous influence of the reaction temperature and the reaction time on the molecular weight of the polymer is pointed out. This property increases when the reaction temperature decreases and the reaction time

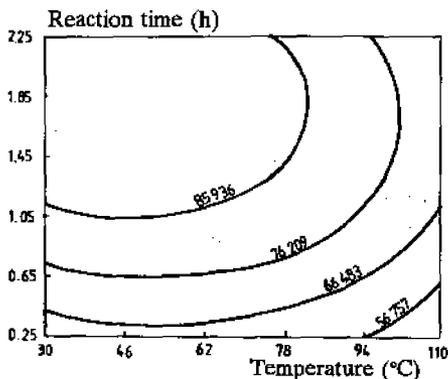


Fig.7. Constant level curves of the molecular weight against reaction temperature (x_1) and reaction time (x_2) (the rest of variables are taken in the middle of their variation domain).

increases, the influence of the second variable being stronger. The stationary point, placed in the experimental domain, is a maxima and its coordinates are $x'_{1s} = 43.6^\circ\text{C}$ and $x'_{2s} = 1.9$ hours (the ' refers to the fact that the property taken into account in this case is the molecular weight).

In Figure 8 constant level curves of the molecular weight of the polymer against the reaction temperature (x_1) and the amount of catalyst are given.

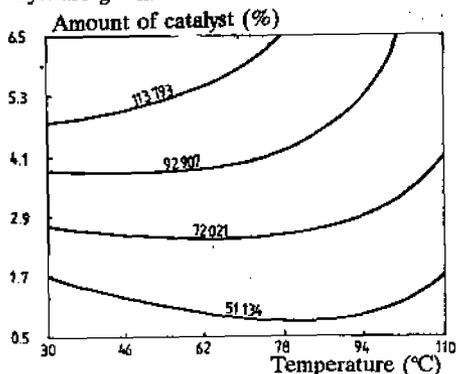


Fig.8. Constant level curves of the molecular weight in the experimental field of the reaction temperature (x_1) and the amount of catalyst (x_3) (the rest of variables are taken in the middle of their variation domain).

Evidently the highest values of the molecular weight are obtained for lower reaction temperatures and larger amounts of catalyst, the influence of the latter one being stronger.

The amount of water strongly influences the molecular weight of the polymer as one may see in Figure 9, in which the response surfaces of this property are presented against x_1 (the reaction temperature) and x_4 (the amount of water). The greater the values of these variables the lower the molecular weight. The stronger influence of these two variables appears in the domain of their higher values.

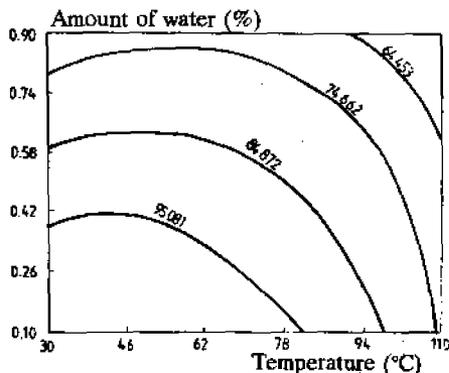


Fig.9. The influence of the reaction temperature (x_1) and the amount of water (x_4) on the molecular weight of the obtained polymer (the rest of variables of variables are taken in the middle of their variation domain).

Two other independent variables (the reaction time and the amount of catalyst) simultaneous influence on the molecular weight is presented in Figure 10.

The greater these variables are, the greater the molecular weight will be, but the influence of the amount of catalyst is stronger.

Figure 11 presents the constant level curves of the molecular weight of the polymer against the reaction time (x_2) and the amount of water (x_4). In order to obtain high values of the molecular weight one must increase the reaction time and decrease the amount of water.

Finally, in Figure 12, the simultaneous

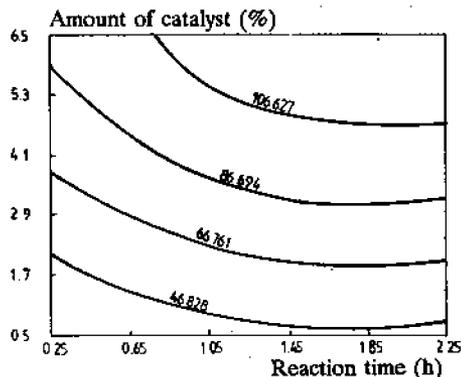


Fig.10. Constant level curves of the molecular weight in the experimental field of the reaction time (x_2) and the amount of catalyst (x_3) (the rest of variables are taken in the middle of their variation domain).

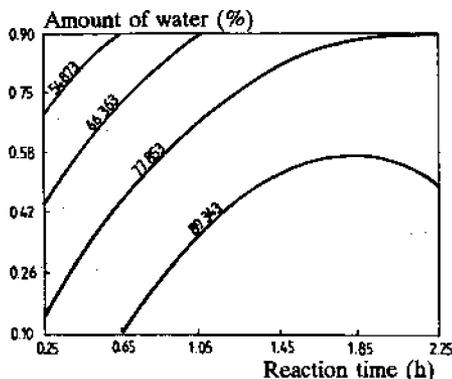


Fig.11. Constant level curves of the molecular weight of the obtained polymer in the experimental field of the reaction time (x_2) and the amount of water (x_4) (the rest of variables are taken in the middle of their variation domain).

influence of the amount of catalyst (x_3) and the amount of water (x_4) on the molecular weight of the polymer is presented.

The first independent variable taken into account in this case strongly influences this property, its increase determining the increase of the molecular

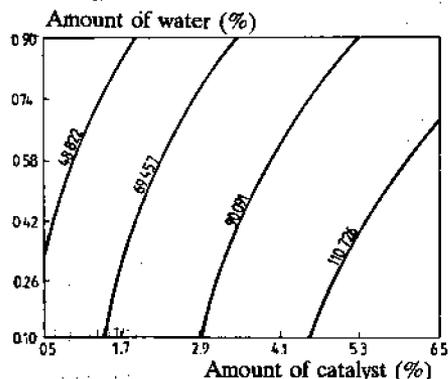


Fig.12. Curves of constant molecular weight yield in the experimental field of the amount of catalyst (x_3) and the amount of water (x_4) (the rest of the variables are taken in the middle of their variation domain).

weight. The increase of the other variable determines the decrease of the molecular weight but, in this case, its influence is not so significant.

Examining these figures one may notice that the amount of catalyst has the strongest influence on the molecular weight of the polymer. High values of this property may be obtained for higher amounts of catalyst, lower reaction temperatures and amount of water and for reaction time long enough.

CONCLUSIONS

An analysis of the experimental results and surface responses leads to the following conclusions.

- High molecular weights of the polymer may be obtained for large amounts of catalyst, lower amounts of water, mean reaction temperatures (about 95°C) and reaction time of about 1.8-2 hours.

- High conversions may be obtained for large amounts of catalyst, too, mean reaction temperatures and reaction time of about 2 hours, the influence of the amount of water being, in this case, insignificant.

- In order to obtain optimum values for both

properties taken into account large amounts of catalyst, low amounts of water, reaction time of about 2 hours and mean reaction temperatures of about 95 °C may be used.

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