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# REACTION CONDITIONS STUDY IN LINEAR H-FUNCTIONAL POLYSILOXANE SYNTHESIS

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## ABSTRACT

A reaction conditions study in the synthesis of methylhydropolysiloxanes was proposed taking into account the variation of some parameters, such as conversion, amount of active hydrogen, intrinsic viscosity, molecular weight versus the reaction time, amount of catalyst and reaction temperature. Methylhydropolysiloxanes were obtained using a bulk heterogeneous polymerization-equilibration reaction of octamethylcyclotetrasiloxane ($D_4$), linear methylhydrosiloxane (L-31) and hexamethyl-disiloxane (HMDS), in the presence of styrene-divinylbenzene sulfonic acid copolymer (VIONI-CS-34C) as catalyst.

## INTRODUCTION

For the preparation of polysiloxane, organic polymers and block copolymers, siloxane copolymers with variable compositions, and controlled molecular weights having Si-H groups in the main chain or on both ends [1, 2] have been synthesized.

Siloxane copolymers with Si-H reactive groups have been obtained through several methods: the cohydrolysis reaction of the various organochlorosilanes with trimethylchlorosilane and methyldichlorosilane [3], the equilibration reaction of octamethylcyclotetrasiloxane ($D_4$) with tetramethylcyclotetrasiloxane $(D^H)_4$ or of the $D_4$ with 1,3-dihydrodisiloxane [4].

There is a sound interest in the aspects related to the mechanism of the polymerization-equilibration reaction, the nature and amount of the catalyst, distribution of the Si - H groups, the relation between viscosity, time and catalyst amount, reproducibility and thermal behavior of the siloxane segments as a function of the reaction conditions [5].

Generally, there have been studies of the thermodynamic and kinetic of polymerization-equilibration reactions by ring opening of the more accessible cyclosiloxanes, i.e., $D_3$ and $D_4$.

Data on the equilibration of hydropolysiloxanes segments are scarce. Due to the instability of the Si-H link in a basic medium [6], copolymerization of the $D_4$ and $(D^H)_4$ cyclics may be achieved only by cationic polymerization, in the presence of acid catalysts such as sulphuric acid, sulfonic acids or ion exchangers in an acid form [7, 8].

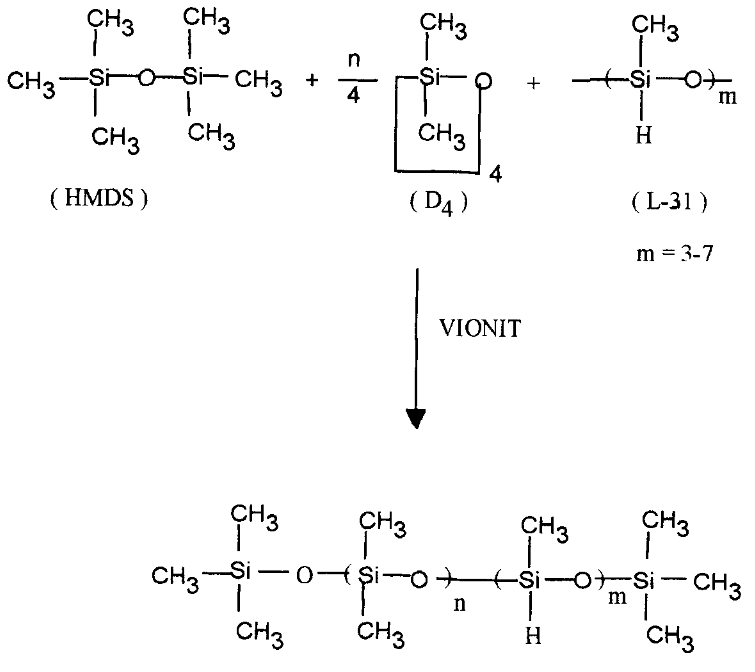
Some kinetic studies on the methylhydrocyclosiloxanes polymerization have been performed in the presence of methanesulfonic acid or with trifluoromethanesulfonic acid in different solvents which allowed us to draw the conclusion that the polymerization rate increases in the following order: $D_5^H < D_4^H < D_6^H < D_7^H$ [8, 9].

The present paper deals with the study of the reaction conditions for the synthesis of methylhydropolysiloxane copolymer, by the polymerization-equilibration reaction of the mixture of linear hydromethylsiloxane and octamethylcyclotetrasiloxane [10]. The copolymer molecular weight may be controlled by the introduction in the polymerization system of determined amounts of a blocking agent, such as hexamethyldisiloxane (HMDS) or 1,3-dihydrodisiloxane.

## EXPERIMENTAL

### Materials

Octamethylcyclotetrasiloxane ($D_4$) 98% purity, $n_D^{20}$ = 1.3982, $d_4^{20}$ = 0.9561g/cm$^3$, (Fluka). Linear hydromethylsiloxane (L -31), with: 1.364% H, $d_4^{20}$ = 0.9977 g/cm$^3$, $n_D^{20}$ = 1.3983, (Union Carbide, USA). Hexamethyldisiloxane (HMDS), 99.5% purity, $n_D^{20}$ = 1.3774, $d_4^{20}$ = 0.7636 g/cm$^3$, (Fluka). An ion exchange resin, styrenedivinylbenzene with sulfonic groups (exchange capacity



Reaction Scheme 1

= 4.2mval/g, porosity = 39.42%, granulation = 0.4-0.65 mm, specific surface = 35m$^2$/g), (VIONIT CS 34C, Romanian product).

## Measurements

The intrinsic viscosities ($\eta^{25}$) for the H-functional polysiloxanes were determined on an Ubbelohde viscometer.

The molecular weight has been determined with the following relation: $M_v^{1/2} = 10^2 \lg\eta / 1.19 - 75.12$ [11].

The amount of active H was determined using a modified Zerewitinoff method [12].

## Synthesis of Linear H-functional Polysiloxane

The linear H-functional polysiloxanes were synthesized through the bulk polymerization-equilibration reaction of linear hydro-methylsiloxane (L-31) with octamethylcyclotetrasiloxane ($D_4$), using hexamethyldisiloxane (HMDS) as end groups capping agent, in the presence of a dried styrenedivinylbenzene with sulfonic groups (VIONIT CS 34C) catalyst (Reaction Scheme 1). The catalyst was dehydrated by azeotropic distillation before addition to the reaction mixture.

The following experimental procedure was used: 76.9 g linear hydromethylsiloxane (L-31), 32.4 g (0.2 mole) hexamethyldisiloxane (HMDS) and 740 g (4.5 mole) octamethyl-cyclotetrasiloxane ($D_4$) were mixed. Molar ratio of $(CH_3)_2Si/HSi(CH_3)$ was 50:5. Measured amounts (50 g) of this mixture were then charged in a 250 ml reaction flask fitted with a dry nitrogen inlet, mechanical stirrer, thermometer and reflux condenser. To obtain the relation between the reaction parameters, the amount of catalyst, reaction temperature and reaction time were varied according to Table 1. After the prescribed reaction time elapsed the catalyst was removed from the reaction mixture through filtration. The traces of the unreacted monomer were finally distilled (150°C, 20 mmHg) from the obtained copolymer. Conversion values were calculated from the (final product)/(initial reaction mixture) ratio.

The resulting copolymer has been characterized by refractive index, intrinsic viscosity, amount of active hydrogen and average molecular weight ($\overline{M}_v$) measurements.

## RESULTS AND DISCUSSION

Table 1 lists the experimental results obtained in the synthesis of siloxane copolymers $(CH_3)_3Si-[OSi(CH_3)_2]_X-[OSiH(CH_3)]_Y-OSi(CH_3)_3$, with Si - H functional groups on the chain, trough a bulk cationic polymerization-equilibration reaction of the mixtures of siloxane cyclics and linear methylhydropolysiloxane oligomers, in the presence of HMDS as a molecular weight regulator and VIONIT CS-34C as catalyst. The $(CH_3)_2SiO/H(CH_3)SiO$ ratio was kept constant to 50/5.

Considering the relation between composition, time, temperature, catalyst concentration, viscosity (molecular weight) and conversion, a study of the conditions required by the polymerization - equilibration reaction was initiated.

The independent variables considered for this study were: reaction time, hour ($x_1$); amount of catalyst, % ($x_2$); reaction temperature, °C ($x_3$).

The following characteristics were taken as dependent variables: conversion, % ($y_1$); amount of H, % ($y_2$); intrinsic viscosity, cSt ($y_3$); refractive index, $n_D^{20}$ ($y_4$); molecular weight, $\overline{M}_v$ ($y_5$). The data from Table 1 was processed by the multiple regression method, which led to equations of the form:

$$y = b_0 + \Sigma\, b_i x_i + \Sigma\, b_{ij} x_i x_j\,,\ i \le j \qquad (1)$$

$$(i = 1\text{-}3;\ j = 1\text{-}27)$$

TABLE 1. The Reaction Conditions and Experimental Data

| No. | Time h | Catalyst % | Temp °C | Conversion % | H % | $\eta^{25}$ cSt | $n_D^{20}$ | $\overline{M}_v$ |
|---|---|---|---|---|---|---|---|---|
| **1** | 0.5 | 2.175 | 90 | 48 | 0.2291 | 39.03 | 1.4010 | 3435 |
| **2** | 1 | 2.5 | 90 | 74 | 0.1592 | 49.96 | 1.4016 | 4572 |
| **3** | 2 | 2.5 | 90 | 86 | 0.1489 | 60.15 | 1.4018 | 5543 |
| **4** | 3 | 2.5 | 90 | 92 | 0.1399 | 62.13 | 1.4019 | 5643 |
| **5** | 4 | 2.5 | 90 | 88 | 0.1374 | 66.71 | 1.4021 | 6110 |
| **6** | 2.5 | 1 | 90 | 64 | 0.2021 | 50.68 | 1.4018 | 4643 |
| **7** | 2.5 | 2 | 90 | 84 | 0.1391 | 61.71 | 1.4021 | 5674 |
| **8** | 2.5 | 3 | 90 | 88 | 0.1358 | 72.023 | 1.4007 | 6556 |
| **9** | 2.5 | 4 | 90 | 88 | 0.1282 | 67.44 | 1.4008 | 6173 |
| **10** | 2.5 | 5 | 90 | 80 | 0.1253 | 74.72 | 1.4008 | 6774 |
| **11** | 2.5 | 2.5 | 50 | 66 | 0.1740 | 43.089 | 1.4001 | 3871 |
| **12** | 2.5 | 2.5 | 70 | 84 | 0.1387 | 58.59 | 1.4002 | 5391 |
| **13** | 2.5 | 2.5 | 90 | 84 | 0.1274 | 64.63 | 1.4002 | 5930 |
| **14** | 2.5 | 2.5 | 110 | 86 | 0.1289 | 65.57 | 1.4002 | 6012 |
| **15** | 2.5 | 2.5 | 30 | 56 | 0.2011 | 36.22 | 1.3986 | 3122 |
| **16** | 0.5 | 1 | 30 | 22 | 0.5046 | 29.038 | 1.3930 | 2286 |
| **17** | 0.5 | 5 | 30 | 32 | 0.3409 | 29.29 | 1.3984 | 2317 |
| **18** | 4 | 1 | 30 | 32 | 0.3684 | 28.309 | 1.3982 | 2198 |
| **19** | 4 | 5 | 30 | 80 | 0.1744 | 58.805 | 1.4000 | 5412 |
| **20** | 0.5 | 1 | 110 | 64 | 0.2745 | 39.758 | 1.3990 | 3514 |
| **21** | 0.5 | 5 | 110 | 86 | 0.1403 | 62.552 | 1.4000 | 5749 |
| **22** | 4 | 1 | 110 | 86 | 0.1528 | 59.325 | 1.4000 | 5459 |
| **23** | 4 | 5 | 110 | 80 | 0.1427 | 65.882 | 1.4002 | 6040 |
| **24** | 2.5 | 2.5 | 70 | 82 | 0.1462 | 60.678 | 1.4002 | 5582 |
| **25** | 2.5 | 2.5 | 70 | 82 | 0.1443 | 61.719 | 1.4002 | 5675 |
| **26** | 2.5 | 2.5 | 70 | 84 | 0.1514 | 61.094 | 1.3949 | 5885 |
| **27** | 2.5 | 2.5 | 70 | 82 | 0.1505 | 60.678 | 1.3949 | 5582 |

where :

$b_0$ - the intercept;
$b_i$ - the linear regression coefficients;
$x_i$ - the independent variables;
$b_{ij}$- non-linear regression coefficients.

Table 2 lists the regression coefficients recorded for all the measured functions. Also, it provides information on the significance of the obtained equations (statistics F and the determination coefficient, $R^2$), as well as the eigenvalues for all matrices of non-linear regression coefficients.

As seen from the analysis of F and $R^2$ values, all equations are significant, the calculated F values being much higher than the tabular F (which, for 3 and 23 degrees of freedom and probability $P = 0.95$, is of 3.03, while, for $P = 0.99$ it is, respectively, 4.76). The same conclusion may also be drawn, when analyzing the values of the determination coefficients, $R^2$, which are close to 0.99.

Analysis of the eigenvalues allows us to draw two important conclusions:

a) all measured properties vary non-uniformly within the experimental field characteristic directions of variation being noticed, which results from the fact that the absolute values of the three eigenvalues are much different;

b) two of the above mentioned properties, i.e. viscosity and molecular weight (actually representing the same characteristic of the polymer) show maxim values as all their eigenvalues are negative.

The response surfaces for the other properties take a saddle-like shape which means that, generally, they evidence no absolute extreme values.

The coordinates of the maxim values for the viscosity and molecular weight functions may be determined from stationary condition:

$$dy / dx_i = 0 \quad \text{----->} \quad b_{ij}\, x^S_i = -\, b_i / 2 \; ; \; i \leq j \qquad (2)$$

Solving for the system of Equation 2 lead to the following vectors:

$$\mathbf{x}^S \Big|_{\eta} = \begin{bmatrix} 5.334 \\ 26.102 \\ 104 \end{bmatrix} \quad (3); \qquad \mathbf{x}^S \Big|_{\overline{M}_V} = \begin{bmatrix} 4.65 \\ 16.73 \\ 92 \end{bmatrix} \quad (4)$$

TABLE 2. The Regression Coefficients for the Five Measured Characteristics, Determined by Processing Data from Table 1

| Variables | | The regression coefficients for | | | | |
|---|---|---|---|---|---|---|
| | | Conversion | % H | $\eta^{25}$ | $n_D^{20}$ | $\overline{M}_v$ |
| | $b_o$ | -47.08119 | 0.8207 | -13.047 | 1.387 | -2102.28 |
| $x_1$ | $b_1$ | 22.50595 | -0.1313 | 12.989 | $1.454x10^{-3}$ | 1303.86 |
| $x_2$ | $b_2$ | 24.06762 | -0.1442 | 4.141 | $2.424x10^{-3}$ | 469.976 |
| $x_3$ | $b_3$ | 1.037717 | $-5.059x10^{-3}$ | 0.877 | $1.402x10^{-4}$ | 94.423 |
| $x_1^2$ | $b_{11}$ | -2.630456 | $1.469x10^{-2}$ | -2.174 | $4.747x10^{-5}$ | -213.850 |
| $x_1x_2$ | $b_{12}$ | 0.064265 | $3.369x10^{-3}$ | 0.3764 | $-1.437x10^{-4}$ | 41.646 |
| $x_2^2$ | $b_{22}$ | -2.53393 | $1.424x10^{-2}$ | -0.1174 | $-1.5x10^{-4}$ | -18.279 |
| $x_1x_3$ | $b_{13}$ | $-5.979x10^{-2}$ | $3.772x10^{-4}$ | $3.633x10^{-3}$ | $-1.096x10^{-5}$ | -0.1198 |
| $x_2x_3$ | $b_{23}$ | $-6.002x10^{-2}$ | $3.165x10^{-4}$ | $-1.92x10^{-4}$ | $-1.153x10^{-5}$ | -0.5603 |
| $x_3^2$ | $b_{33}$ | $-2.177x10^{-3}$ | $1.084x10^{-5}$ | $-4.286x10^{-3}$ | $-3.013x10^{-7}$ | -0.4567 |
| | F | 233 | 186 | 274 | $1.637x10^{6}$ | 234 |
| | $R^2$ | 0.992 | 0.989 | 0.993 | cca.1 | 0.992 |
| | $\lambda_1$ | $6.74x10^{-4}$ | $1.786x10^{-2}$ | $-4.276x10^{-3}$ | $1.233x10^{-4}$ | -0.4116 |
| | $\lambda_2$ | -2.504 | $1.109x10^{-2}$ | $-5.066x10^{-2}$ | $5.819x10^{-7}$ | -9.819 |
| | $\lambda_3$ | -2.663 | $-2.767x10^{-6}$ | -2.241 | $-2.267x10^{-4}$ | -222.349 |

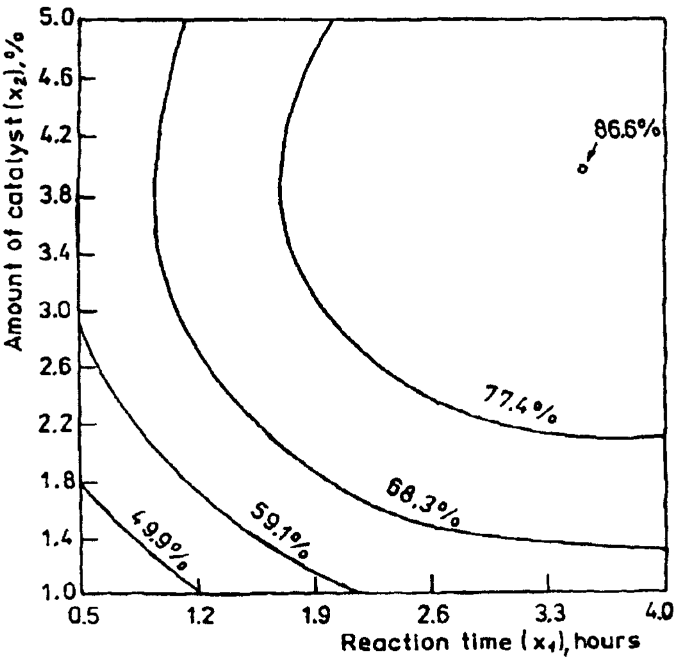


**Figure 1.** Constant level curves of conversion in the experimental field of the reaction time ($x_1$) and the amount of catalyst ($x_2$).

As seen from the coordinates analysis, the points of extreme are to be found outside the experimental domain, the amount of catalyst being exaggeratelly high as compared with the applied maximum value (5%). Consequently, one may say that the molecular weight increases in the experimental field up to a relatively maximum value, found on the domain's border.

For a simpler illustration of the independent variables' influence upon the studied properties, in the following the constant-level curves for the response surfaces in the planes of each two variable are presented. As for each property, three such plots may be drawn, only the most representative ones will be analyzed.

Figures 1-3 show the constant level curves for the monomer conversion; generally, it increases with the increase of the three experimental parameters taken into account. In the time-catalyst concentration domain (Figure 1), a maximum conversion of 86.6% may be observed at about 3.5 hours and 3.9% catalyst. The fact that, over these values, a slight conversion decrease is

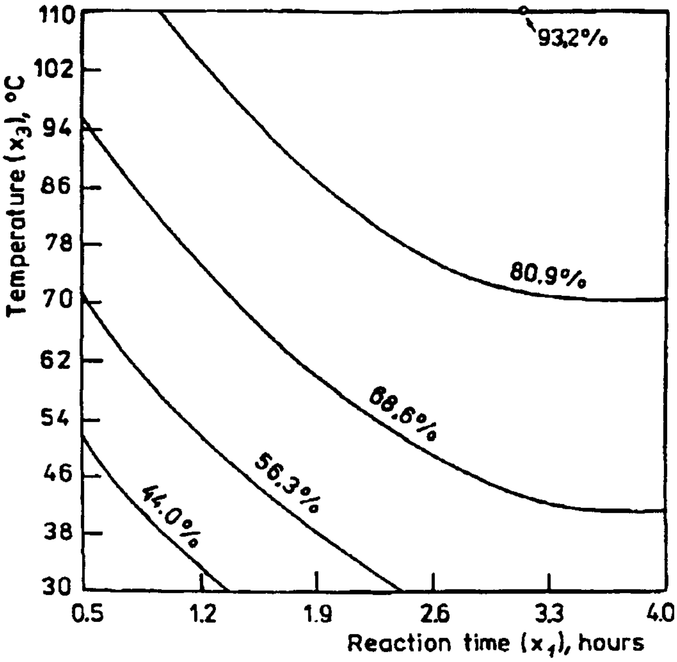


Figure 2. Constant level curves of conversion in the experimental field of the reaction temperature ($x_3$) and the reaction time ($x_1$).

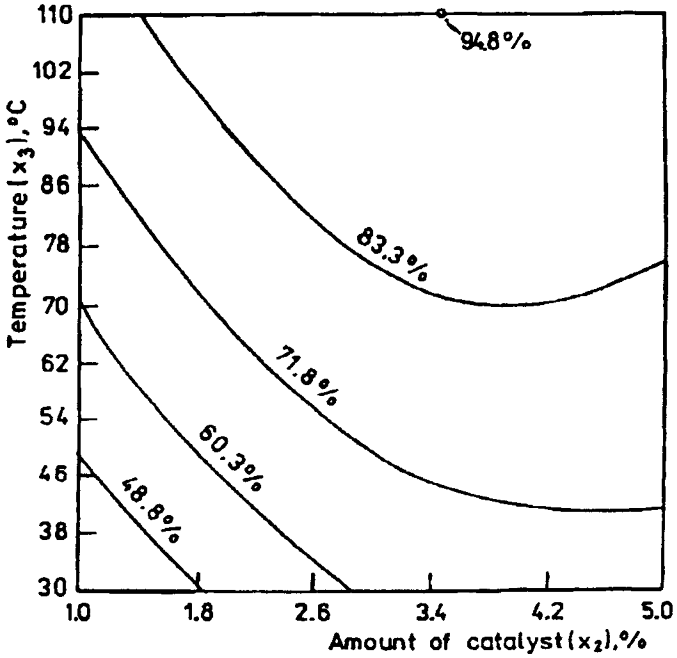


Figure 3. The influence of the reaction temperature ($x_3$) and the amount of catalyst ($x_2$) on conversion.

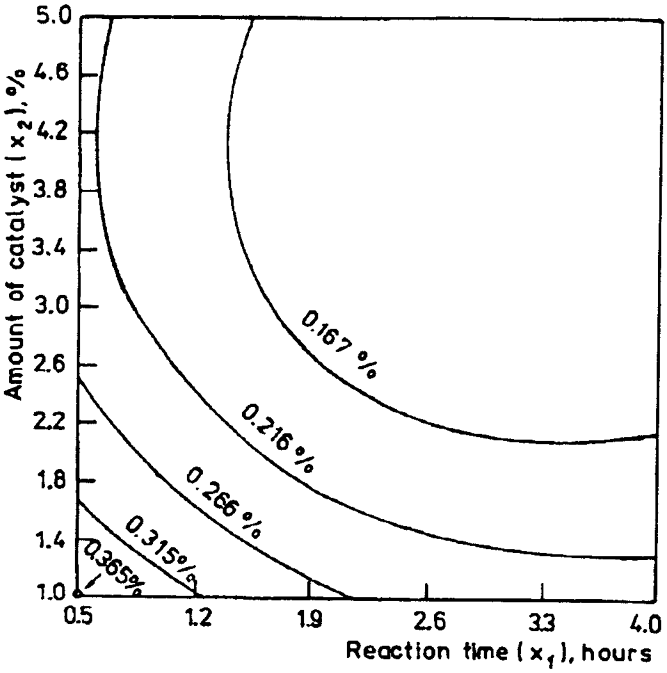


**Figure 4.** Constant level curves of the response surface for the content of active hydrogen in the polymer in the experimental field of the reaction time ($x_1$) and the amount of catalyst ($x_2$).

observed may be explained by the equilibrium character of the polymerization-equilibration reaction.

Analysis of the three figures also show that the influence of the three factors taken into study is much higher for low values and that this influence becomes smaller as their values are higher. Therefore the polymerization process is more stable, from the viewpoint of the monomer consumption, at high values of the reaction parameters.

Figures 4 to 6 represent the response surface for the content of active hydrogen in the polymer. An opposite trend is shown, as compared with conversion, which may be explained by the higher reactivity of the L-31 linear oligomer versus cycles $D_4$, which agrees with the findings of the Graczyk on the study of cycles $D_4$ and $D_4^H$ polymerization kinetics [9] . Thus, at reduced values of the parameters defining the reaction conditions, time, temperature and the amount of catalyst, breaking of the $D_4$ cyclics is more difficult, the obtained copolymer heaving less $D_4$ unit and a higher hydrogen content.

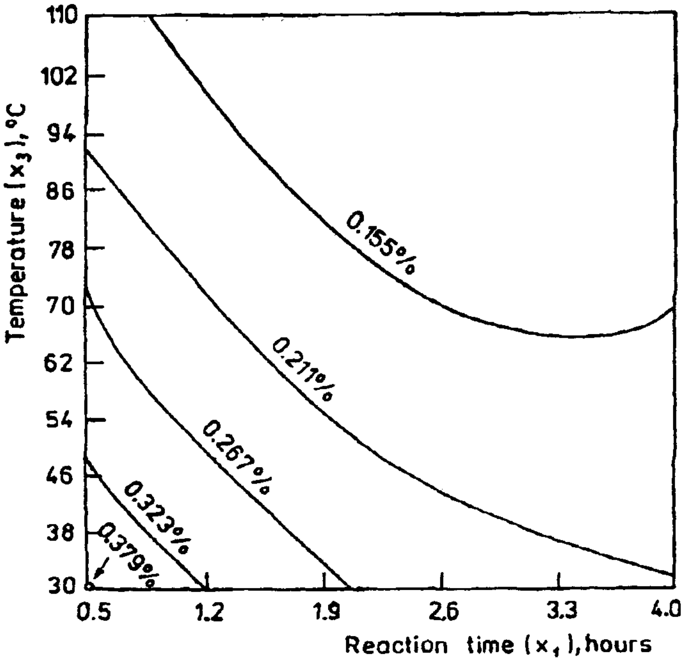


Figure 5. The influence of the reaction temperature ($x_3$) on the content of active hydrogen in the obtained polymer.

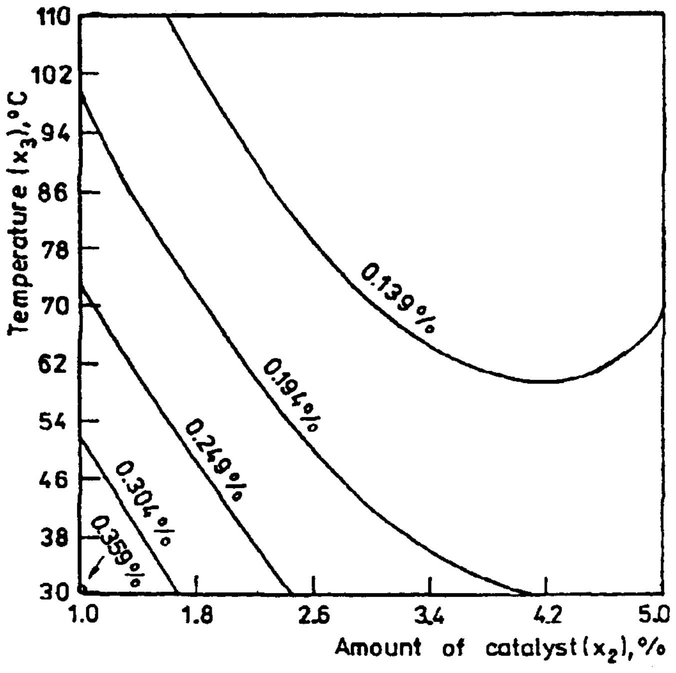


Figure 6. Constant level curves of the response surface for the content of active hydrogen in the final polymer in the experimental field of the amount of catalyst ($x_2$) and the reaction temperature ($x_3$).

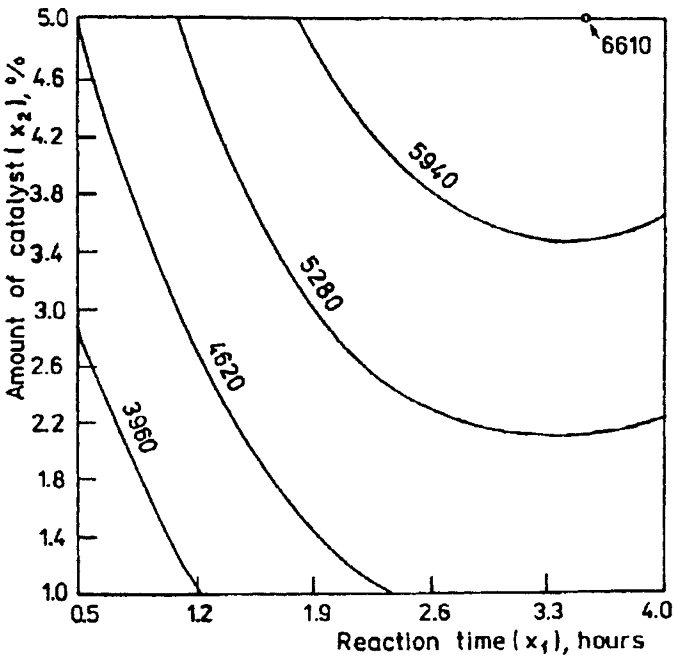


**Figure 7.** Constant level curves for the polymer's molecular weight in the experimental field of the reaction time ($x_1$) and the amount of catalyst ($x_2$).

Finally, Figures 7 to 9 present the constant level curves for the response surface of the polymer's molecular weight in the three experimental fields. In this case, too, the three parameters have a positive influence on the polymer molecular weight. Higher increases are recorded for lower values of the variables taken into study. When keeping the catalyst addition constant at a level of 2.5% (Figure 8), a maximum of the molecular weight-of about 5970, at about 3.4 hours and 102°C is recorded. Again, one may assume that this maximum is determined by the equilibrium character of the polymerization process.

## CONCLUSION

Analysis of the experimental results and of the constant level curves permits drawing of the following conclusions: the monomer conversion increases with the increase of the three parameters: time, temperature and amount of catalyst; also, an opposite tendency of the three independent parameters influence on the amount of active hydrogen from the polymer may be observed, as induced by the difference of reactivity between cycles ($D_4$) and linear

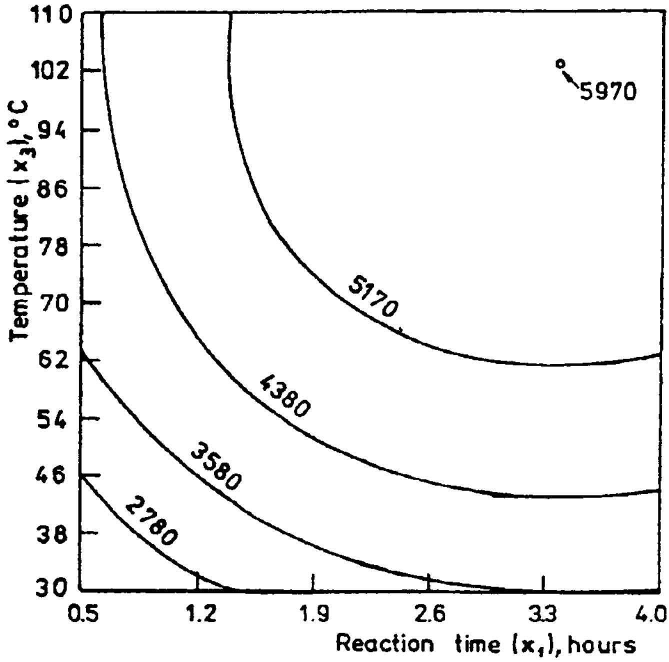


Figure 8. The influence of the reaction time ($x_1$) and the reaction temperature ($x_3$) on the polymer's molecular weight.

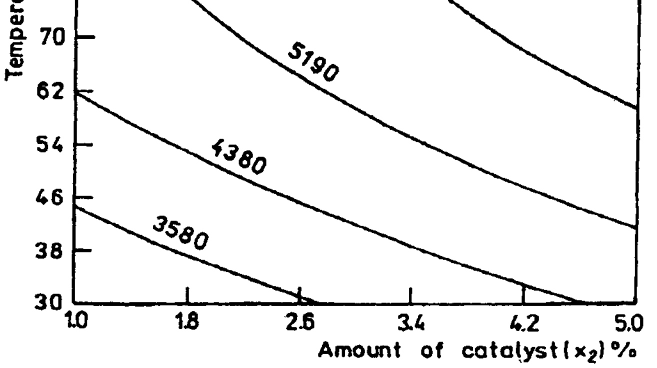


Figure 9. Constant level curves of the polymer's molecular weight against amount of catalyst ($x_2$) and reaction temperature ($x_3$).

methylhydrosiloxane (L-31); the polymer molecular weight is positively influenced by the increase of the three independent parameters, especially at their low values.

## REFERENCES

[1] W. Noll, The Chemistry of Silicones, Academic Press, New York (1968).

[2] I. Yilgör and J. E. McGrath, *Adv. Polym. Sci., 88*, 1 (1988).

[3] J. Heimberger, H. Sheerschmidt, and K. Rühlmann, *Plaste und Kautschuk, 25,* 386 (1978).

[4] S. Schindler and K. Rühlmann, *Plaste und Kautschuk, 25*, 384 (1978).

[5] P. M. Sormani, R. J. Minton, I. Ylgör, P. J. Andolino, J. S. Riffle, C. Tran, and J. E. McGrath, *Polym. Prepr., 25 (1)*, 227 (1984).

[6] J. D. Summers, C. S. Elsbernd, P. M. Sormani, P. J. A. Brandt, C. A. Arnold, I. Yilgör, J. S. Riffle, S. Kilic, and J. E. McGrath in *"Inorganic and Organometallic Polymers"*, M. Zeldin, Ed., ACS Symposium, Series 360, Washington, DC, Chap. 14 (1988).

[7] H. Hamann, K. Michael, I. Spirin, and G. Tschernko, *Plaste und Kautschuk, 25*, 380 (1978).

[8] S. P. Gupta, M. Moreau, M. Masure, and P. Sigwalt, *Eur. Polym. J., 29(1)*, 15 (1993).

[9] T. Graczyk and Z. Lasocki, *Bull. Acad. Pol. Sci., 27*, 185 (1979).

[10] D. Giurgiu, V. Hamciuc, N. Chelaru, and L. Pricop, Rom. Pat., 105814 $B_1$ (Cl. C 08 G 77/04), (1990).

[11] M. Marcu, S. Lazarescu, and M. Cazacu, *Materiale Plastice, 27(4)*, 212 (1990).

[12] I. Urbanski, W. Czerwinski, K. Janicka, F. Majewska, H. Zowall, and G. Gordon Cameron, Transl. Ed., *Handbook of Analysis of Synthetic Polymers and Plastics*, Ellis Horwood, England, Chapter 20 (1979).

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