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Polymerization of Methyl Methacrylate Initiated with Invertase and $FeCl_3$ in Water

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SUMMARY

The polymerization of methyl methacrylate initiated by a system consisting of invertase, ferric chloride and water was investigated at room temperature. Second order, central, composite, rotatable experimental design was used in order to perform the work.

INTRODUCTION

In some previously published papers, IMOTO et al. reported the aqueous solution polymerization of methyl methacrylate (MMA) using an initiation system consisting of α-amylase (or lysozyme) and copper(II) ion (IMOTO et al., 1977; IMOTO et al., 1978), or of nylon 3 and copper(II) ion (IMOTO et al., 1976). The authors proposed a possible mechanism of polymerization involving the formation of chelate bonds between the copper(II) ion, the monomer, water molecule and the electron-donating oxygen atoms in the protein (polyamide) chain. These unconventional polymerizations were performed at elevated temperatures (60 - 80°C) and were proved to be of radical nature.
The present paper is concerned with the unconventional polymerization of methyl methacrylate in aqueous solution, in presence of invertase and ferric chloride, carried out at room temperature; the study was performed by using second order, central, composite, rotatable experimental design.

EXPERIMENTAL

Materials and polymerization procedure

Invertase (β-D-fructofuranoside:fructohydrolase; E.C. 3.2.1.26) was a commercial product prepared by Serva, ca. 3U/mg (one unit catalyzes the hydrolysis of 1 mole sucrose per minute at 55°C, pH 4.5). MMA was purified by usual methods. Highly pure commercial ferric chloride was used without further purification.
MMA and the reagents were placed in long reaction am-

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poules (6 ml monomer and 18 ml aqueous solution of invertase and ferric chloride), connected to a high vacuum line, frozen in liquid nitrogen, evacuated twice at 10^{-2} Torr and sealed. The enzyme dissolved only in water. The ampoules were shaken at room temperature (mild shaking, 6 shakings/7 sec. every 15 min.). After reaction the contents of the ampoules were poured in large amounts of methanol to precipitate the polymer. After filtration the products were kept in hot water for seven hours, to remove the enzyme, dried in vacuo, and weighed. No grafting of invertase with MMA was observed.

Molecular weight determination

The number-average degree of polymerization was determined by using the WELCH's (1962) equation (benzene, 30°C):

$$\log \bar{P}_n = 3.346 + 1.32 \log[\eta]$$

Experimental design

To carry out the work, the second order, central, composite, rotatable experimental design was used (COCHRAN and COX, 1968). The advantages of this method are the following ones:

- the number of experiments is reduced, a fact which results in the reduction of the amounts of materials, energy and time spent, so that the experimental part of the work is done in optimum conditions,
- the regression equation obtained by data processing is defined on the whole experimental field, and
- the complexity of calculation of regression coefficients is reduced due to the orthogonality of many independent variables vectors.

Actual independent variables were transformed according to the following formula:

$$x_i = (X_i - X_{ic})/\Delta X_i \qquad (1)$$

where

x_i - encoded variable, dimensionless
X_i - actual variable
X_{ic} - central value for "i" variable
ΔX_i - factorial interval for "i" variable.

Variable transformation is given in Table 1, and experimental conditions are listed in Table 2.

Data processing

The experimental results were processed by using multiple regression method in order to obtain response surfaces in the form

$$Y = a_o + \Sigma a_i x_i + \Sigma a_{ij} x_i x_j \qquad i \leq j \qquad (2)$$

where a_i and a_{ij} are the regression coefficients for the property Y. To perform the calculus, standard subroutines, which compute regression coefficients from

TABLE 1

Transformation of variables

Coded values / Actual values	-1.682	-1	0	1	1.682
Polymerization period (h)	1.00	7.082	16	24.91	31.00
$FeCl_3$ content (g)	0.0001	0.002	0.005	0.0079	0.01
Invertase cont. (g)	0.01	0.41	1.00	1.59	2.00

TABLE 2

Experimental design and experimental results

	Experimental design			Experimental results	
	x_1	x_2	x_3	Conversion (%)	$\bar{M}_n$
1	-1	-1	-1	2.760	726,380
2	1	-1	-1	8.515	2,686,200
3	-1	1	-1	4.433	182,413
4	1	1	-1	4.950	3,680,545
5	-1	-1	1	0.254	649,603
6	1	-1	1	3.250	3,528,689
7	-1	1	1	16.660	476,550
8	1	1	1	63.045	1,714,800
9	1.682	0	0	27.610	3,352,848
10	-1.682	0	0	0.353	1,140,210
11	0	1.682	0	17.550	1,812,300
12	0	-1.682	0	0.085	98,015
13	0	0	1.682	37.157	653,750
14	0	0	-1.682	0.014	389,011
15	0	0	0	29.183	431,223
16	0	0	0	34.600	895,357
17	0	0	0	26.740	561,162
18	0	0	0	43.480	331,903
19	0	0	0	40.081	471,807
20	0	0	0	37.720	503,415
21	0	0	0	36.511	569,100

x_1 - polymerization period (in coded values)
x_2 - $FeCl_3$ content (in coded values)
x_3 - Invertase content (in coded values)

equation (2), together with the statistics necessary to test their significance and the regression significance were used.

The obtained response surfaces were studied to give the influence of reaction parameters (polymerization duration, ferric chloride content and enzyme content) on the room temperature aqueous solution polymerization of MMA.

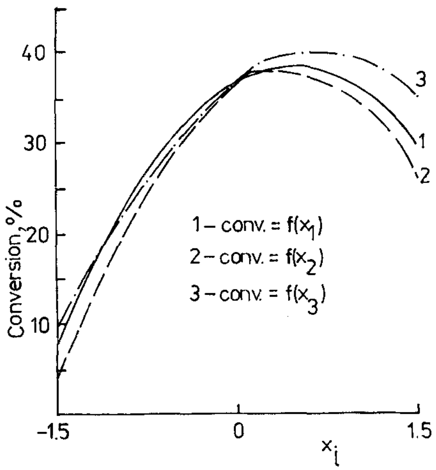

Figure 1.
Variation of conversion versus polymerization period, $FeCl_3$ content and invertase content.

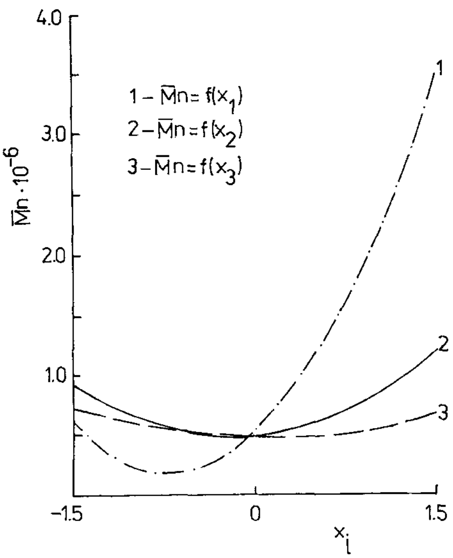

Figure 2.
Variation of molecular weight versus polymerization period, $FeCl_3$ content and invertase content.

RESULTS AND DISCUSSION

To understand the influence of the studied parameters on the progress of the polymerization process, Figures 1 and 2 present the variation of one characteristic (conversion and molecular weight, respectively) versus a parameter, all the others being taken at values corresponding to the center of the experimental field. The shape of all these curves suggests the existence of extreme values of conversion and molecular weight in the experimental field studied. To clarify this observation, the curves of constant properties were plotted in the experimental field of two parameters (x_1,

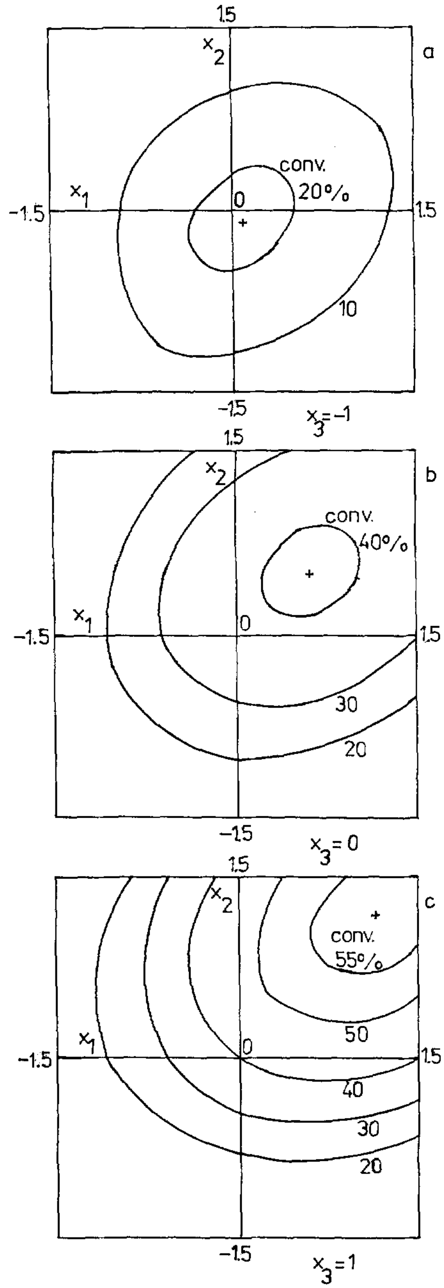

Figure 3.
Variation of conversion in the field of polymerization period (x_1) and ferric chloride content (x_2) for
a - x_3= -1
b - x_3= 0
c - x_3= 1
x_3 being invertase content. Extrema coordinates:
a - x_1= 0.102
x_2=-0.102
conv. 21.58%
b - x_1= 0.627
x_2= 0.539
conv. 41.28%
c - x_1= 1.151
x_2= 1.164
conv. 57.15%

x_2), the third one being taken at three different values (see Table 1) (Figure 3 and Figure 4).
The shape of the curves showing the variation of conversion, as well as of those showing the variation of the molecular weight in the experimental field of x_1 and x_2 confirm the existence of extreme values of both conversion and molecular weight. Extreme coordinates were found by the derivation of the response surfaces and solving the resulted system of linear simultaneous equations; the obtained values of x_1, x_2, conversion or molecular weight are given for each distinct case.

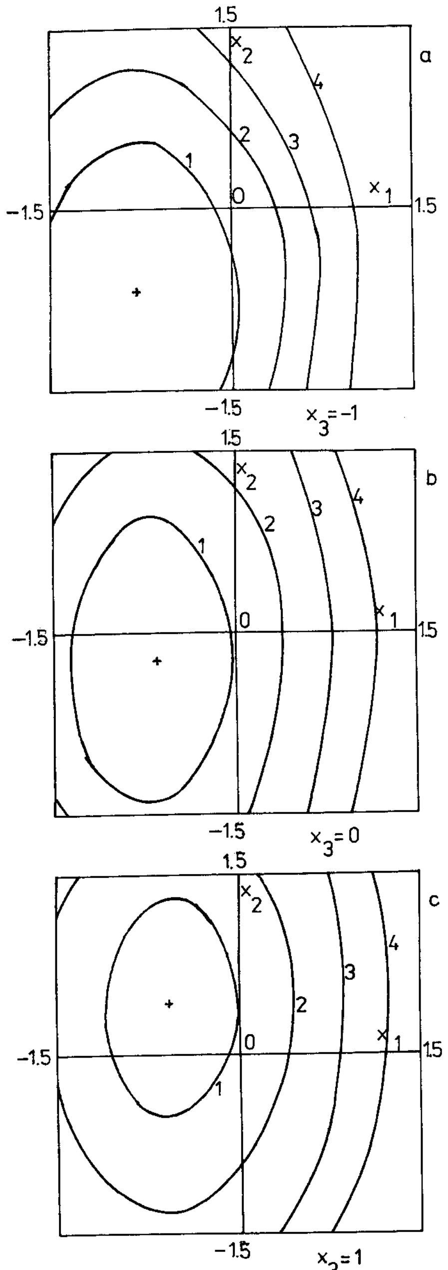

Figure 4.
Variation of molecular weight in the field of polymerization period (x_1) and and ferric chloride content (x_2) for
a - x_3= -1
b - x_3= 0
c - x_3= 1
x_3 being invertase content.

a - 1 $\bar{M}_n = 5\cdot10^5$
2 $\bar{M}_n = 1\cdot10^6$
3 $\bar{M}_n = 1.5\cdot10^6$
4 $\bar{M}_n = 2.5\cdot10^6$

b - 1 $\bar{M}_n = 5\cdot10^5$
2 $\bar{M}_n = 1\cdot10^6$
3 $\bar{M}_n = 1.75\cdot10^6$
4 $\bar{M}_n = 2.5\cdot10^6$

c - 1 $\bar{M}_n = 5\cdot10^5$
2 $\bar{M}_n = 1\cdot10^6$
3 $\bar{M}_n = 1.75\cdot10^6$
4 $\bar{M}_n = 2.5\cdot10^6$

Extrema coordinates:

a - x_1=-0.829
x_2=-0.868
$\bar{M}_n$=-10,478

b - x_1=-0.700
x_2=-0.220
$\bar{M}_n$=165,772

c - x_1=-0.570
x_2= 0.416
$\bar{M}_n$=353,098

Figure 3 shows that the evolution of the conversion is influenced by both x_1 and x_2, while Figure 4 shows that the main parameter influencing the molecular weight evolution is x_1.
The slight decrease of molecular weight values, as indicated by the first parts of the curves in Figure 2 (starting from x_1=-1.5), as well as the slight decrease of conversion values, as indicated by the last parts of the curves in

Figure 1 (starting from x_i=0) could be due to a regression error arising from different experimental errors in different points. This hypothesis is confirmed by the extrema coordinates of the molecular weight (Figure 4, a; $\bar{M}_n$ calculated has a negative value), at least in one case. However, the experimental field was correctly chosen, as proved by the existence of extreme values around the center of the field. The experimental parameters (polymerization period, ferric chloride content, invertase content) were also well chosen, as confirmed by the important values obtained for both conversion and molecular weight.

CONCLUSION

By using second order, central, composite, rotatable experimental design, the influence of polymerization period, ferric chloride and invertase contents on the room temperature aqueous solution polymerization of methyl methacrylate was studied. The optimum experimental conditions were established; the mentioned polymerization process yields high molecular weight polymers, the conversion reaching more than 50% in some cases. Considering that the monomer does not polymerize in water, at room temperature, it clearly appears that the polymerization process is initiated by the presence of ferric chloride - invertase system.
Research in progress will be published in the future.

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