

# Ce(IV)-Ion-Initiated Grafting of Methyl Methacrylate onto Gelatin

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## Synopsis

Grafting of methyl methacrylate onto gelatin in the presence of Ce(IV) ions as graft initiators has been studied. By statistical planning of experiments regression equations were obtained which described the effect of gelatin, methyl methacrylate, and initiator concentrations on the grafting efficiency, gelatin, and methyl methacrylate conversion and on the copolymer composition.

## INTRODUCTION

Ce(IV) salts belong to the class of redox agents which initiate grafting. In the presence of organic substances behaving as reducing constituents in the system, one-electron transfer is effected:



If the reducing constituent is a macromolecular substance, radicals are formed on the polymeric chain and, in the presence of the vinyl monomer, a highly efficient graft reaction is accomplished. The Ce(IV) salt initiating effects were discovered in 1958,<sup>1</sup> and in a short time this method has been adopted for grafting on various polymers, e.g., cellulose<sup>2</sup> or wool.<sup>3</sup>

Grafting of collagenous proteins initiated by Ce(IV) salts has been reported by Rao et al.<sup>4-11</sup> They grafted various acrylates onto tropocollagen, untanned hide powder, and some modified collagens under nitrogen and found both the graft yield and efficiency high in comparison with other initiation systems. Factors affecting mainly the grafting efficiency are both monomer and initiator concentrations. The graft yield increases with the monomer concentration only up to a certain limiting value and then decreases, due to the higher extent of homopolymerization, while higher initiator concentrations affect grafting adversely by inhibitive effects.

The grafting mechanism of acrylic monomers onto collagen initiated by Ce(IV) ions is given particular attention in the paper by Prentiss et al.<sup>12</sup> As a result of extensive experiments, a reaction mechanism has been suggested, and factors having potential influence on both the yield and efficiency of the process [pH, temperature, concn. of acrylate and Ce(IV) salt] have been studied. Grafting takes place even in the presence of oxygen, and the cerium content in the substrate has no substantial effect on the process.

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Gelatin as collageneous substrate and Ce(IV) ions as initiators for methyl methacrylate (MMA) were used in this work. Parameters affecting predominantly the grafting process have been investigated, namely, the effects of gelatin, MMA, and initiator concentrations in the mixture of the grafting efficiency and both gelatin and MMA conversions. The method of statistical planning of experiments, adopted for evaluation<sup>13-15</sup> enabled the determination of interdependent effects of all three factors investigated.

The aim of this paper is solely the determination of the effects on the factors investigated in the grafting, without qualitative evaluation of the resulting product, which could be presumably useful for leather filling, surface finishing, or other applications in the leather industry.

## EXPERIMENTAL

### Material

Edible commercial gelatin was grafted with MMA prepared from the commercial stabilized monomer by repeated shaking with 10% solution of sodium carbonate, 1% sodium hydroxide solution, and water, drying with anhydrous calcium chloride and distillation. Cerium-ammonium nitrate, analytical grade, was from VEB Jenapharm-Laborchemie Apolda (GDR). Other analytical grade chemicals, obtained from various suppliers, were used without further treatment.

### Grafting

Reactions were performed in a three-neck flask, placed in a constant temperature bath (35°C) with a stirrer and inert gas (carbon dioxide) supply which was connected to the vacuum source. Weighed portions of gelatin (Table II), dissolved in 75 mL of distilled water, were poured into the flask. Five mL of 0.1M nitric acid and required amounts of Ce(IV) salt (Table II) dissolved in 10 mL of 0.1M nitric acid were added. The solution was deaerated by repeated evacuation and introduction of carbon dioxide atmosphere into the flask, under continuous stirring at 35°C. Then required MMA portions (Table II) were added, the flask content was increased up to 100 mL volume with degassed distilled water, and the mixture was stirred for 4 h at 35°C.

### Separation of Products

The reaction solution was neutralized with sodium carbonate and precipitated by the addition of 200 mL of methanol. Further treatment of the reaction mixture is given in a flow scheme (Fig. 1).

The contents of dissolved gelatin in supernatants, designated  $G_1$  to  $G_3$ , was determined by photometry at 540 nm after reaction with biuret reagent. The homopolymer contents in the chloroform extracts  $H_1$  and  $H_2$  (Soxhlett apparatus) was determined by weighing the evaporation residue. This residue contains only insignificant traces of proteins (determined by Kjeldahl method). The insoluble portion  $C$  was the copolymer, and its yield was determined by weighing after drying at 100°C.

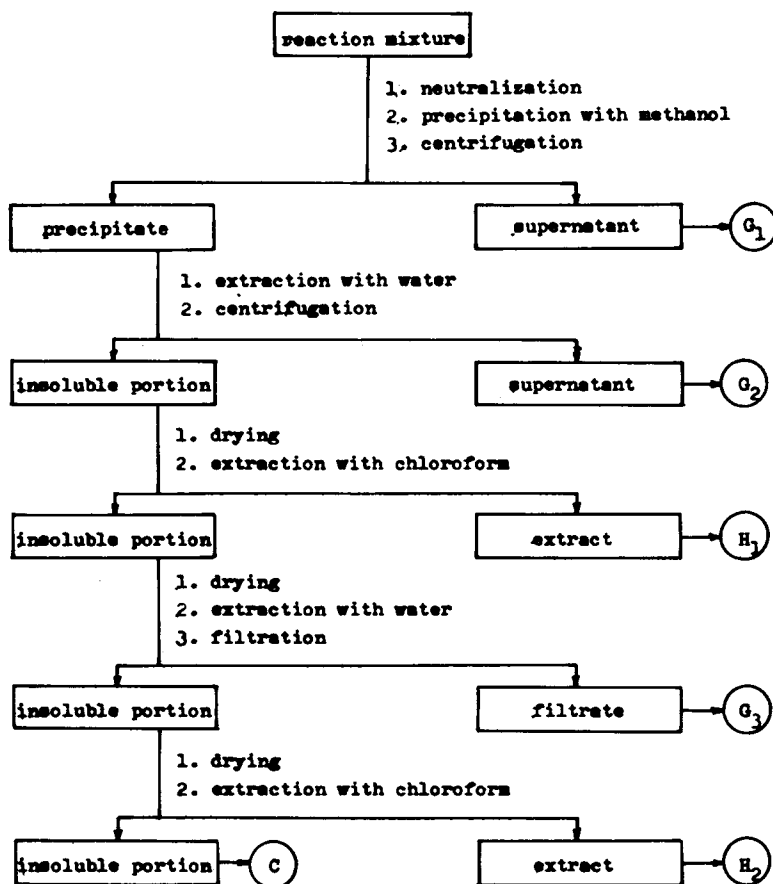


Fig. 1. Schematic diagram of separation of constituents from the mixture after MMA grafting onto gelatin.

### Definitions

All the concentration data below are given in percentage (w/v); the concentration of Ce(IV) ions is expressed also in  $\text{mol}\cdot\text{L}^{-1}$ .

**Independent variables ( $x_i$ ).**  $x_1$  = gelatin concentration,  $x_2$  = MMA concentration, and  $x_3$  = Ce(IV) salt concentration.

**Dependent variables ( $y_i$ ).**  $y_1$  = grafting efficiency (%) [defined by eq. (2)],  $y_2$  = gelatin conversion (%) [defined by eq. (3)],  $y_3$  = MMA to homopolymer conversion (%) [eq. (4)],  $y_4$  = MMA to copolymer conversion (%) [eq. (5)],  $y_5$  = total MMA conversion (%) [=  $y_3 + y_4$ , eq. (6)], and  $y_6$  = MMA contents in the copolymer (%) [eq. (7)].

$$y_1 = \frac{C - (x_1 - G)}{H + C - (x_1 - G)} \times 100 (\%) \quad (2)$$

$$y_2 = \frac{x_1 - G}{x_1} \times 100 (\%) \quad (3)$$

$$y_3 = \frac{H}{x_2} \times 100 (\%) \quad (4)$$

$$y_4 = \frac{C - (x_1 - G)}{x_2} \times 100 (\%) \quad (5)$$

$$y_5 = y_3 + y_4 (\%) \quad (6)$$

$$y_6 = \frac{C - (x_1 - G)}{C} \times 100 \quad (7)$$

where  $H$  = concentration of MMA homopolymer (=  $H_1 + H_2$ ; see Fig. 1),  $G$  = concentration of unreacted gelatin (=  $G_1 + G_2 + G_3$ ; see Fig. 1), and  $C$  = copolymer concentration in the reaction mixture.

## RESULTS AND DISCUSSION

Principal factors which may affect the grafting process are the concentrations of gelatin, MMA, and Ce(IV) salt. Other factors like pH value, the presence of salts, and temperature are, according to the data reported in the bibliography, of minor importance and we have, therefore, chosen to keep them constant. The reaction time has been limited to 4 h, which, according to the published data and preliminary experiments, seems to be sufficient. The mathematical model adopted for the description of  $y_i$  functions, characterizing the reaction, was a second degree polynomial, as follows:

$$y_i = b_0 + b_1\bar{x}_1 + b_2\bar{x}_2 + b_3\bar{x}_3 + b_{11}\bar{x}_1^2 + b_{22}\bar{x}_2^2 + b_{33}\bar{x}_3^2 + b_{12}\bar{x}_1\bar{x}_2 + b_{13}\bar{x}_1\bar{x}_3 + b_{23}\bar{x}_2\bar{x}_3 \quad (8)$$

where the values  $\bar{x}_i$  are coded levels of the individual independent variables  $x_i$ . The experiment for this nonlinear mathematical model was planned using a central composite rotatable design of second degree for three factors. The concentration range in which the individual independent variables  $x_i$  should be included were chosen in agreement with the published data<sup>4-12</sup> and preliminary experiments. In the case of gelatin, the upper concentration is limited by gel formation at experimental temperature. Conversion of coded  $\bar{x}_i$  values to the original  $x_i$  value is given in Table I.

The choice of dependent variables was made in order to obtain the maximum information on the effect of the reaction conditions on both efficiency and yield of the process. They are grafting efficiency ( $y_1$ ), gelatin conversion ( $y_2$ ), MMA conversion ( $y_3$  to  $y_5$ ), and poly(MMA) contents in the copolymer ( $y_6$ ). Their

TABLE I  
Relation between Original and Coded Independent Variables  $x_i$

Factor	Unit	$\bar{x}_i$ level				
		$-\alpha$	-1	0	+1	$+\alpha$
$x_1$	% (w/v)	0.5	0.804	1.25	1.696	2.0
$x_2$	% (w/v)	0.5	2.02	4.25	6.48	8.0
$x_3$	% (w/v)	0.0548	0.1534	0.3014	0.4490	0.5480
$x_3$	$\times 10^{-3}$ mol/L	1.0	2.82	5.5	8.18	10.0

TABLE II  
Values of Dependent Variables  $y_i$  Computed from Experimental Results

Experiment no.	Gelatin ( $x_1$ , %)	MMA ( $x_2$ , %)	Ce(IV) salt ( $x_3$ , %)	$y_1$ (%)	$y_2$ (%)	$y_3$ (%)	$y_4$ (%)	$y_5$ (%)	$y_6$ (%)
1	0.804	2.02	0.1534	43.35	51.75	45.54	33.47	79.01	62.02
2	1.696	2.02	0.1534	52.79	43.88	26.73	29.90	56.63	44.74
3	0.804	6.48	0.1534	41.44	35.25	8.02	5.67	13.69	56.62
4	1.696	6.48	0.1534	60.67	25.88	5.40	8.33	13.73	55.10
5	0.804	2.02	0.4490	41.24	73.13	53.96	37.87	91.83	56.66
6	1.696	2.02	0.4490	25.83	52.41	62.38	21.73	84.11	30.01
7	0.804	6.48	0.4490	55.23	46.63	44.75	55.20	99.95	90.56
8	1.696	6.48	0.4490	60.03	63.29	33.33	50.06	83.39	75.09
9	0.5	4.25	0.3014	81.22	57.60	15.29	66.16	81.45	90.70
10	2.0	4.25	0.3014	70.73	62.65	29.18	70.52	99.70	70.52
11	1.25	0.5	0.3014	54.31	32.48	36.00	42.80	78.80	34.52
12	1.25	8.0	0.3014	75.79	48.00	23.88	74.75	98.63	90.88
13	1.25	4.25	0.0548	27.27	11.62	4.70	1.76	6.46	41.66
14	1.25	4.25	0.5480	37.94	28.16	62.68	39.71	102.29	82.75
15	1.25	4.25	0.3014	77.67	43.76	22.35	77.71	100.06	85.79
16	1.25	4.25	0.3014	79.81	47.36	20.70	81.83	102.53	85.45
17	1.25	4.25	0.3014	77.21	52.00	23.06	78.12	101.18	83.63
18	1.25	4.25	0.3014	72.18	43.52	26.35	68.38	94.73	84.23
19	1.25	4.25	0.3014	71.92	42.88	28.23	72.33	99.56	85.15
20	1.25	4.25	0.3014	74.22	50.96	24.92	71.83	96.77	82.73

TABLE III  
Coefficients of Regression Equation Type (8)<sup>a</sup>

Regression coefficient	$y_1$	$y_2$	$y_3$	$y_4$	$y_5$	$y_6$
$b_0$	75.78820	46.43530	24.06710	75.58430	99.48340	84.75730
$b_1$	(0.10367)	(-0.93770)	(-0.07813)	(-1.08662)	(-1.16559)	-6.94623
$b_2$	6.68457	(-1.75851)	-8.60351	3.66339)	-4.91549	13.08790
$b_3$	(0.22164)	7.79984	15.10260	11.08040	26.17070	7.53866
$b_{11}$	(-1.79990)	6.70779	(0.57518)	-6.04180	-5.39725	-3.19789
$b_{22}$	-5.66341	(-0.32435)	3.29999	-9.42260	-6.09038	-9.53159
$b_{33}$	-17.13730	-7.52093	4.62614	-22.87510	-18.19900	-9.70665
$b_{12}$	3.62500	4.48500	(-0.45625)	(2.15375)	(1.69750)	3.36750
$b_{13}$	-5.03500	(1.64750)	(2.30375)	(-2.54625)	(-0.24250)	-2.91500
$b_{23}$	5.15250	(2.36000)	2.57375	11.87870	14.45250	9.25250
Index of correlation $I(\bar{x}, y)$	0.954680	0.846711	0.925695	0.940892	0.939598	0.959200

<sup>a</sup> Values in parentheses are, according to the absolute value of the  $T$  criterion, statistically insignificant.

TABLE IV  
Coordinates of Stationary Points  $\bar{x}_{i(s)}$  and Values of  $y_i$  Functions in Stationary Points

Function	$y_1$	$y_2$	$y_3$	$y_4$	$y_5$	$y_6$
$\bar{x}_{1(s)}$	0.9118	0.0984	16.7275	-0.0917	0.0020	-1.0238
$x_{1(s)}$ (%)	1.6567	1.2934	8.7105	1.2091	1.2509	0.7934
$\bar{x}_{2(s)}$	0.8845	-0.2615	5.2951	0.40673	0.8505	1.0001
$x_{2(s)}$ (%)	6.2224	3.6668	16.0581	5.1560	6.1466	6.4802
$\bar{x}_{3(s)}$	0.0055	0.4882	-7.2703	0.3528	1.0567	1.0187
$x_{3(s)}$ (mmol/L)	5.5147	6.8084	0	6.4455	8.3319	8.2285
$y_{i(s)}$ (%)	78.79	48.52	-54.26	78.33	111.22	98.70
Type of extreme	Maximum	Minimax	Minimum	Maximum	Maximum	Maximum

values have been computed from experimental data using eqs. (2)–(7), respectively. Results are given in Table II. Coefficients of regression equations (8) have been computed using the Hewlett-Packard 2100 A computer; a survey of computed regression coefficients and correlation indices is given in Table III. The validity of regression equations is limited to the experimental range of  $x_i$  values (Table I) and should not be extrapolated beyond this region without further verification.

An important variable describing the grafting process is the grafting efficiency ( $y_1$ ), defined as the ratio of monomer reacted to copolymer to the total monomer reacted. This value is affected by all the  $x_i$  parameters; the effect of gelatin concentration ( $x_1$ ) seems to be of minor importance. The stationary point of the  $y_1$  function lies within the experimental region (Table IV) and the maximum value of the function is 78–79%. Effects of monomer ( $x_2$ ) and initiator ( $x_3$ )

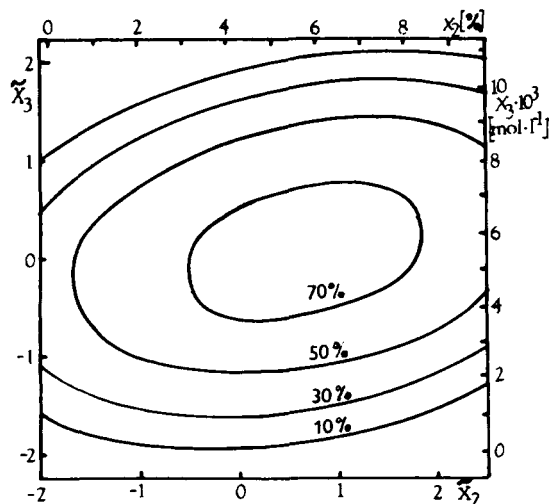


Fig. 2. Contour lines for grafting efficiency ( $y_1$ ) as a function of MMA ( $x_2$ ) and initiator ( $x_3$ ) concentrations, at constant gelatin concentration ( $x_1 = 1.696\%$ ).

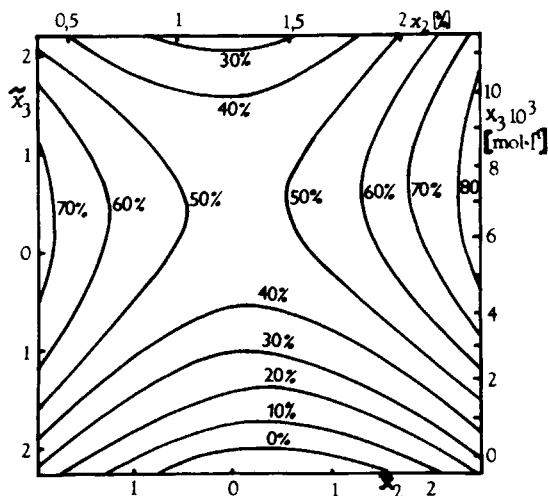


Fig. 3. Contour lines for gelatin conversion ( $y_2$ ) as a function of gelatin ( $x_1$ ) and initiator ( $x_3$ ) concentrations, at constant monomer concentration ( $x_2 = 4.25\%$ ).

concentrations, respectively, on the grafting efficiency can be seen in Figure 2 showing a plot of the function  $y_1 = f(x_2, x_3)$  at a constant concentration of gelatin 1.7%, close to the coordinate  $\bar{x}_{1(s)}$  of the stationary point.

The value of gelatin conversion ( $y_2$ ) is important with respect to the initial material utilization. This value is not markedly affected by MMA concentration (Table III). An increase in the gelatin concentration ( $x_1$ ) affects the conversion positively, the most important being, however, the Ce(IV) salt concentration. The stationary region of the  $y_2$  function is characterized by a minimax with coordinates close to the center of the experiment (Table IV). The function  $y_2$

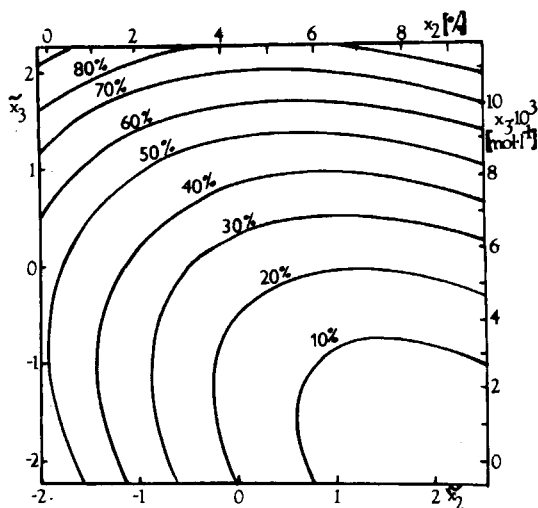


Fig. 4. Contour lines for MMA to homopolymer conversion ( $y_3$ ) as a function of MMA ( $x_2$ ) and initiator ( $x_3$ ) concentrations, at constant gelatin concentration ( $x_1 = 0.804\%$ ).



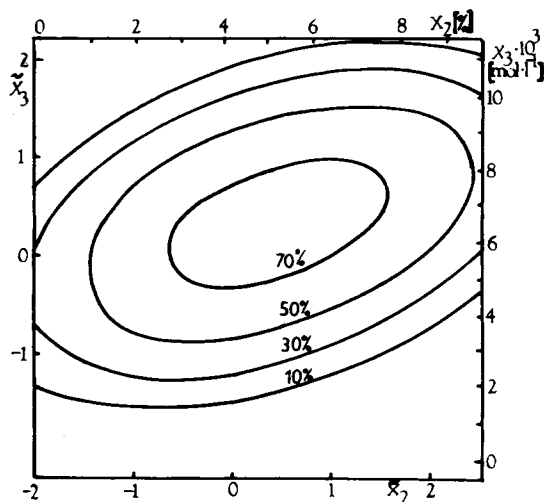


Fig. 5. Contour lines for MMA to graft copolymer conversion ( $y_4$ ) as a function of MMA ( $x_2$ ) and initiator ( $x_3$ ) concentrations, at constant gelatin concentration ( $x_1 = 1.25\%$ ).

$= f(x_1, x_3)$  at the MMA concentration 4.25% (Fig. 3) exerts a rising trend when proceeding on the constant gelatin concentration ca. 1.3% towards the center of the experiment; after reaching the minimax, the function keeps rising on the constant initiator concentration ca.  $7 \text{ mol} \cdot \text{L}^{-1}$  towards higher and lower gelatin concentrations ( $x_1$ ), respectively. With respect to gelatin concentration, ( $y_2$ ) the best suitable Ce(IV) salt concentration should be  $7 \text{ mol} \cdot \text{L}^{-1}$ . A further conversion rise can be achieved by either increasing or reducing the gelatin concentration ( $x_1$ ).

However, MMA grafting onto the gelatin substrate is accompanied by its si-

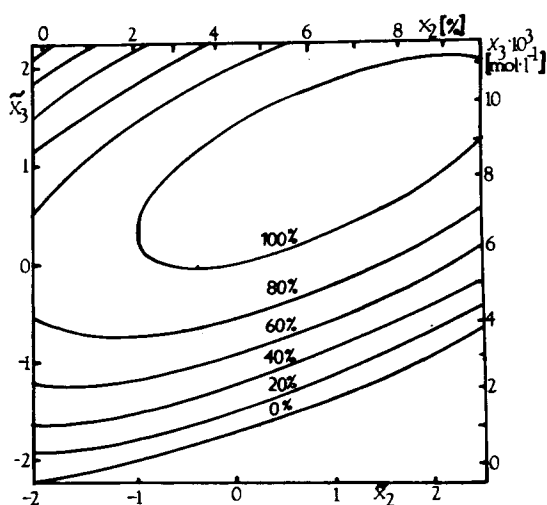


Fig. 6. Contour lines for total MMA conversion ( $y_5$ ) as a function of MMA ( $x_2$ ) and initiator ( $x_3$ ) concentrations, at constant gelatin concentration ( $x_1 = 1.25\%$ ).

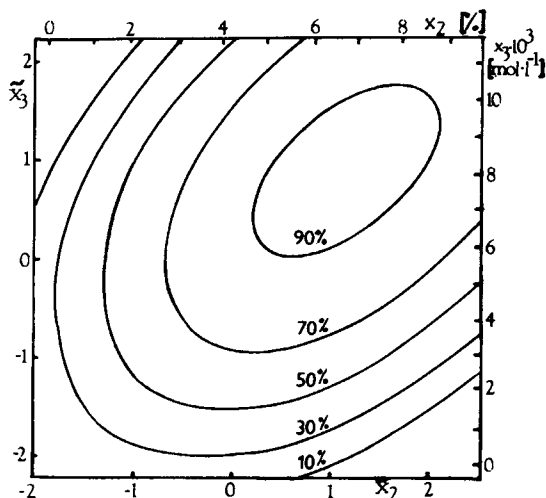


Fig. 7. Contour lines for poly(MMA) contents in the graft copolymer ( $y_6$ ) as a function of MMA ( $x_2$ ) and initiator ( $x_3$ ) concentrations, at constant gelatin concentration ( $x_1 = 1.25\%$ ).

multaneous homopolymerization. The homopolymer is produced solely by the chain transfer mechanism; preliminary experiments in the absence of gelatin yielded no homopolymer. According to the regression coefficient values of the  $y_3$  function (Table III), gelatin concentration in the reaction mixture ( $x_1$ ) has no effect on the homopolymer formation. The  $y_3$  function has a minimal effect; its coordinates (Table IV) are, however, beyond the experimental region. Effects of monomer ( $x_2$ ) and initiator ( $x_3$ ) concentrations on the extent of homopolymerization, at constant gelatin concentration ( $x_1$ ), are shown in Figure 4. It results from the plot that the homopolymerization can be minimized (<10%) at higher monomer concentrations (>6%) with substantial simultaneous reduction of Ce(IV) ion concentration (<3 mmol·L<sup>-1</sup>) in the solution. This observation is in agreement with the results reported by Rao et al.<sup>5,6</sup> [increased homopolymerization with increasing Ce(IV) ions concentration above 2.5 mmol·L<sup>-1</sup>]. Positive effects of increased monomer concentration on the suppression of homopolymerization have been observed only in the lower concentration region; at higher concentrations of MMA (above 5–7.5%) this effect is negative. It is in agreement with published results.<sup>5,6</sup>

MMA to graft copolymer conversion, characterized by the  $y_4$  function (Table III) is significantly affected by all the independent variables  $x_i$ , the gelatin concentration variations ( $x_1$ ) being of least importance. The  $y_4$  function has a maximum at 78.3% (defined by coordinates, Table IV), located in the center of the experiment. The plot of the  $y_4$  function at constant gelatin concentration 1.25% (corresponding approximately to the stationary point) is shown in Figure 5.

The dependence of the overall MMA conversion on the  $x_i$  variables is described by the  $y_5$  function, defined by the sums of  $y_3 + y_4$  values in the individual experimental points. The highest theoretical value, 111.2% is reached at  $\bar{x}_i$  values (Table IV). The region of 100% monomer conversion is rather wide and shifted towards higher values of  $x_2$  and  $x_3$  variables (Fig. 6).

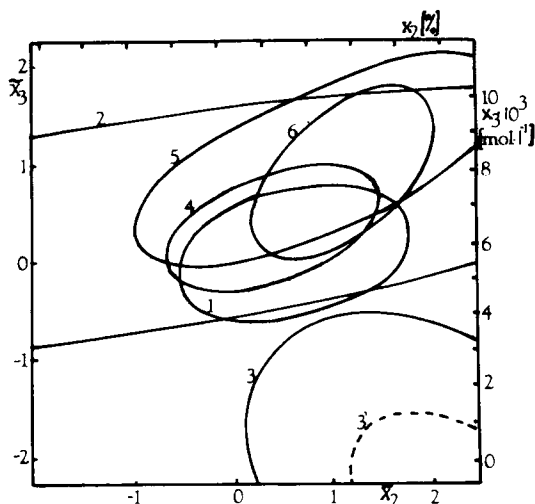


Fig. 8. Contour lines of optimum values of dependent variables  $y_i$  as functions of MMA ( $x_2$ ) and initiator ( $x_3$ ) concentrations, at gelatin concentration of 1.25% (1 -  $y_1$  = 70%, 2 -  $y_2$  = 40%, 3 -  $y_3$  = 10%, 3' -  $y_3$  = 0%, 4 -  $y_4$  = 70%, 5 -  $y_5$  = 100%, 6 -  $y_6$  = 90%).

Finally, the poly(MMA) contents in the graft copolymer is described by the function  $y_6$ , which is significantly influenced by all the independent variables  $x_i$  investigated (Table III). Unlike the case of the other dependent variables  $y_i$ , the aim is not to obtain a maximum (Table IV) or minimum value of the function; the  $y_6$  value required depends on the application of the graft product, which is beyond the scope of this paper. For illustration see Figure 7, a plot of the  $y_6$  function for various MMA ( $x_2$ ) and Ce(IV) ion ( $x_3$ ) concentrations at constant gelatin concentration (1.25%).

Gelatin concentration has only a slight effect on the  $y_i$  variables and its upper limit is restrained for experimental reasons to values below 2%. Therefore, effects of MMA and Ce(IV) ion concentrations on the  $y_i$  variables are plotted at constant gelatin concentrations, 1.25% and 1.7%, respectively (Figs. 8 and 9). Contour lines in Figures 8 and 9 define the regions of maximum (in case of  $y_3$  minimum)  $y_i$  values obtainable. There is no superposition of all the respective areas, and, thus, it is impossible to find conditions providing maximum (or minimum) values for all the  $y_i$  dependent variables. In practice, it is important to get 100% monomer conversion. The 100% level of this variable, characterized by the function  $y_5$ , covers a fairly high portion of the experimental region. At gelatin concentration of 1.25% (Fig. 8), only 40% of gelatin conversion can be obtained in the region of 100% MMA conversion. When the gelatin concentration is increased to 1.7% (Fig. 9), we get partial superposition of 100% MMA and 60% gelatin conversion regions, and in the entire 100% per cent MMA conversion region the gelatin conversion is above 50%. With respect to the original material utilization, regions in the neighborhood of 8% of MMA and 8–9 mmol·L<sup>-1</sup> of Ce<sup>4+</sup> salt should be preferred. However, there is rather high MMA homopolymerization (>20%) in this region (Fig. 9). A reduction of homopolymerization is possible by decreasing of Ce(IV) ion concentration; this induced, however, lower original material utilization. The transition area between the maximum MMA

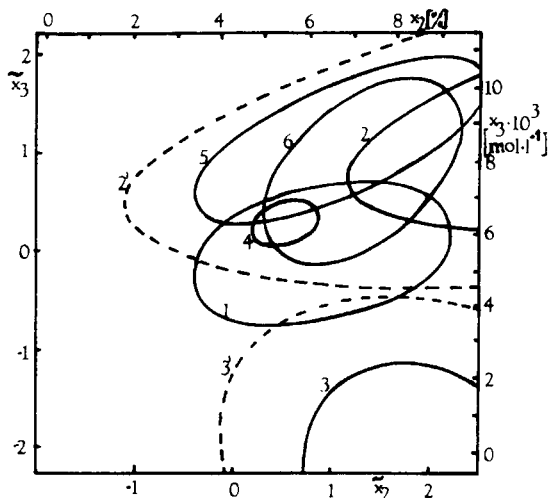


Fig. 9. Contour lines of optimum values of dependent variables  $y_i$  as functions of MMA ( $x_2$ ) and initiator ( $x_3$ ) concentrations, at gelatin concentration of 1.7%; ( $1 - y_1 = 70\%$ ,  $2 - y_2 = 60\%$ ,  $2' - y_2 = 50\%$ ,  $3 - y_3 = 0\%$ ,  $3' - y_3 = 10\%$ ,  $4 - y_4 = 70\%$ ,  $5 - y_5 = 100\%$ ,  $6 - y_6 = 80\%$ ).

and gelatin conversion region and minimum homopolymer yield includes maximum grafting efficiency ( $y_1$ ) and maximum yield of copolymer ( $y_4$ ) regions, both of them plotted by 70% contour line. Locations of both latter regions are very similar, in agreement with the assumption that at 100% MMA conversion the functions  $y_1$  and  $y_4$  should be identical.

The validity of the mathematical model describing the grafting reaction has been checked by experiments in random experimental points. Results (Table V) show that there is good treatment between theory and experiment.

## CONCLUSION

The effect of reaction conditions on methyl methacrylate grafting onto collagenous proteins has been studied using a model system MMA-gelatin-Ce(IV) salt.

From the results obtained by statistical planning of experiments, it can be concluded that the grafting process is significantly affected by concentrations of all reactants in the system. The relatively low effect of gelatin concentration can be explained by the narrow concentration range necessary for experimental reasons. Regression equations have been derived describing relationships between reaction constituent concentrations ( $x_i$ ) and the results of the grafting process ( $y_i$ ). Computed values of the independent variables  $x_i$  corresponding to the  $y_i$  function maxima or minima are different for the individual  $y_i$  variables. There is no such region of reaction conditions covering the optimum values of all  $y_i$  variables involved. It is thus necessary either to choose the region close to the optimum of this  $y_i$  variable, which is of major importance in the particular case (and to accept less satisfactory values of other variables), or to perform optimization for several variables. This can be motivated by various practical (nature of the product) and economical (utilization of original material) reasons.

TABLE V  
Comparison of Computed and Measured  $y_i$  Values: Control of Validity of the Regression Equations Derived

Experiment no.	1	2	3	4
$\bar{x}_1$	0	0	1	1
$x_1$ (%)	1.25	1.25	1.7	1.7
$\bar{x}_2$	0.78	-0.112	1.23	0.336
$x_2$ (%)	6	4	7	5
$\bar{x}_3$	0.668	-0.687	0.668	-0.687
$x_3$ (%)	0.4	0.2	0.4	0.2
$y_1$ (%)				
Computed	72.74	67.12	70.47	67.96
Measured	64.22	63.58	71.24	64.83
Difference	-8.52	-3.54	0.77	-3.13
$y_2$ (%)				
Computed	44.00	42.02	43.57	40.55
Measured	50.08	40.72	49.70	45.12
Difference	6.08	-1.30	6.13	4.57
$y_3$ (%)				
Computed	32.72	17.40	32.73	12.82
Measured	28.50	22.75	28.28	15.84
Difference	4.22	5.35	-4.45	3.02
$y_4$ (%)				
Computed	76.08	57.55	72.77	54.60
Measured	48.73	57.27	70.07	50.82
Difference	27.35	-0.28	-2.70	-3.78
$y_5$ (%)				
Computed	108.80	74.95	105.50	67.23
Measured	77.23	80.02	98.35	65.43
Difference	-31.57	5.07	-7.15	-1.80
$y_6$ (%)				
Computed	94.68	80.12	94.72	76.18
Measured	82.36	81.82	85.30	73.22
Difference	-12.32	1.70	-9.42	-2.96

Some possibilities have been suggested in the discussion. The optimization can also be made by a purely mathematical procedure,<sup>13-15</sup> where the optimum of some key variable with simultaneous limiting conditions for other  $y_i$  variables is chosen.

This work should be considered as an informative study showing joint effects of several parameters, characterizing graft reaction conditions, on original material conversion and both yield and character of the product. In comparison with conventional procedures, the statistical planning of experiments offers considerable time savings. All the found results correspond essentially to those described in the literature; the main success of this communication lies in their quantification.

### References

1. G. Mino and S. Kaizerman, *J. Poly Sci.*, **31**, 242 (1958).
2. J. C. Arthur, Jr., *J. Macromol. Sci.-Chem.*, **A10**(4), 653 (1976).
3. P. L. Nayak, *J. Macromol. Sci., Rev. Macromol. Chem.* **C14**(2), 193 (1976).
4. K. P. Rao, K. T. Joseph, and Y. Nayudamma, *Leather Sci. (Madras)*, **14**, 73 (1967).

5. K. P. Rao, K. T. Joseph, and Y. Nayudamma, *Leather Sci. (Madras)*, **15**, 92 (1968).
6. K. P. Rao, K. T. Joseph, and Y. Nayudamma, *Das Leder*, **19**, 77 (1968).
7. K. P. Rao, K. T. Joseph, and Y. Nayudamma, *Leather Sci. (Madras)*, **16**, 401 (1969).
8. K. P. Rao, K. T. Joseph, and Y. Nayudamma, *J. Polym. Sci. A-1*, **9**, 3199 (1971).
9. K. P. Rao, K. T. Joseph, and Y. Nayudamma, *J. Appl. Polym. Sci.*, **16**, 975 (1972).
10. K. P. Rao, K. T. Joseph, and Y. Nayudamma, *Leather Sci. (Madras)*, **19**, 27 (1972).
11. K. P. Rao, D. H. Kamat, K. T. Joseph, M. Santappa, and Y. Nayudamma, *Leather Sci. (Madras)*, **21**, 111 (1974).
12. W. C. Prentiss, T. W. Hutton, and S. N. Lewis, *J. Am. Leather Chem. Assoc.*, **71**, 111 (1975).
13. W. G. Cochran and G. M. Cox, *The Design of Experiments*, 2nd ed., Wiley, New York, 1957.
14. G. M. Cox, *Planning of Experiments*, Wiley, New York, 1958.
15. D. P. Lambrakis, "Experiments with  $p$ -Component Mixtures," *J. Roy. Stat. Soc. Ser. B*, **30**, 1 (1968).

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