Bisulfite–Persulfate-Initiated Grafting of Methyl Methacrylate onto Gelatin

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Synopsis

Grafting of methyl methacrylate onto gelatin, initiated by the bisulfite–persulfate redox system, has been studied. Using the method of statistical planning of experiments, regression equations have been obtained describing the effects of the methyl methacrylate concentration and the composition of initiating system on the factors characterizing the grafting reaction. Possibilities of the reaction conditions optimalization are discussed.

INTRODUCTION

While grafting of vinyl monomers onto leather, leather powder, or collagen fibers is intensively studied,[1-13] there is only a very limited knowledge concerning the grafting of vinyl monomers on partially degraded collagen, such as gelatin or glue. Grafting of various acrylates on these substances can have some perspective with regard to the utilization of the grafting products in the technology of leather processing, e.g., for finishing or for filling chrome-tanned leathers.

In our previous work[14] we dealt with grafting of methyl methacrylate (MMA) onto gelatin using Ce(IV) ions as initiator. This initiator is very effective (the effectiveness of grafting was up to 78%). There is a drawback in the fact that grafting should be carried out in a highly acid medium (pH < 2) and the respective product gets a yellow tint; also stability of resulting emulsion is not too high. For this reason we tried[15] to do grafting of MMA onto gelatin using the bisulfite–persulfate initiation system. Statistical processing of the grafting results using a linear five-factor mathematical model has shown[15] that the statistically important are the concentrations of MMA and of both components of the initiation system, whereas the temperature (within the range of 20–80°C) and the concentration of gelatin (within the range of 1–4 %) have no statistically important influence. But it has been stated that the linear model is not suitable for describing the reaction. We are, therefore, presenting in this work the results of measuring the influence of the three mentioned, statistically important variables on various reaction parameters using a nonlinear mathematical model.

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EXPERIMENTAL

Material

Edible commercial gelatin has been grafted with the MMA prepared from the commercial stabilized monomer using the alkali extraction and distillation. Other analytical grade chemicals obtained from various suppliers have been used without any further treatment.

Grafting

Reactions have been performed at constant temperature of 35°C in a three-neck flask with a stirrer and carbon dioxide supply. The solution of gelatin (3 g in 90 mL of distilled water) has been poured into the flask and deaerated by repeated evacuation and introduction of carbon dioxide under continuous stirring. Required amounts (Table I) of potassium persulfate ($K_2S_2O_8$) and MMA have been added and the flask content has been filled up to 100 mL volume with deaerated distilled water. After 15 min the required amount (Table I) of sodium bisulfite ($NaHSO_3$) has been added and the mixture has been stirred for 4 h. The reaction mixture has been mixed thereafter with 200 mL of methanol. The further treatment of the reaction mixture is given in a flow scheme (Fig. 1). The content of the dissolved gelatin in the supernatants designated G_1–G_3 has been determined photometrically at 540 nm after the reaction with a biuret reagent. The homopolymer content in the chloroform extracts H_1 and H_2 (in Soxhlett apparatus) has been determined by weighting of the evaporation residue. This residue contains only some insignificant traces of proteins (determined by the Kjeldahl method), which have been omitted for calculation. The insoluble part C has been considered as copolymer and its yield has been determined be weighting after being dried at 100°C.

Definitions

All concentration data mentioned below are given in percentage (w/v).

Independent Variables ($\mathbf{x}_i$). x_1 = MMA concentration, x_2 = $K_2S_2O_8$ concentration, x_3 = $NaHSO_3$ concentration.

Dependent Variables ($\mathbf{y}_i$). y_1 = grafting efficiency (%) [defined by eq. (1)], y_2 = gelatin conversion (%) [defined by eq. (2)], y_3 = MMA to homopolymer conversion (%) [defined by eq. (3)], y_4 = MMA to copolymer conversion (%) [defined by eq. (4)], y_5 = total MMA conversion (%) [defined by eq. (5)], and y_6 = poly(methyl methacrylate) (PMMA) content in the copolymer (%) [defined by eq. (6)]:

$$y_1 = \frac{C - (G_0 - G)}{H + C - (G_0 - G)} \times 100\,(\%) \tag{1}$$

$$y_2 = \frac{G_0 - G}{G_0} \times 100\ \%) \tag{2}$$

$$y_3 = \frac{H}{x_1} \times 100\,(\%) \tag{3}$$

TABLE I
Results of the MMA Grafting onto Gelatin

Experiment no.	x_1, MMA (%)	x_2, $K_2S_2O_8$ (%)	x_3, $NaHSO_3$ (%)	y_1 (%)	y_2 (%)	y_3 (%)	y_4 (%)	y_5 (%)	y_6 (%)
1	2.013	0.262	0.0565	14.34	15.73	82.46	13.56	96.02	37.06
2	4.986	0.262	0.0565	14.03	20.43	84.53	13.77	98.30	52.84
3	2.013	0.738	0.0565	12.73	13.17	83.45	12.17	95.62	38.25
4	4.986	0.738	0.0565	6.26	20.76	31.08	20.05	51.13	23.09
5	2.013	0.262	0.1635	21.95	13.13	77.00	21.65	98.65	52.53
6	4.986	0.262	0.1635	17.05	20.76	48.73	8.16	56.89	39.51
7	2.013	0.738	0.1635	2.05	14.83	83.04	1.74	84.78	7.29
8	4.986	0.738	0.1635	7.63	7.33	75.21	6.22	21.43	58.49
9	1.000	0.500	0.1100	25.03	8.10	62.00	16.70	78.70	40.73
10	6.000	0.500	0.1100	3.92	11.00	81.67	3.33	85.00	37.73
11	3.500	0.100	0.1100	12.45	16.40	51.33	7.30	58.63	47.10
12	3.500	0.900	0.1100	2.68	8.13	68.57	1.89	70.46	21.29
13	3.500	0.500	0.0200	25.00	16.67	64.28	21.42	85.70	60.00
14	3.500	0.500	0.2000	2.30	8.30	86.28	2.03	88.31	22.18
15	3.500	0.500	0.1100	6.81	16.77	80.85	5.91	86.76	29.15
16	3.500	0.500	0.1100	5.62	17.87	78.57	4.62	83.25	23.42
17	3.500	0.500	0.1100	5.41	20.47	82.85	4.74	87.59	21.28
18	3.500	0.500	0.1100	7.33	23.70	74.00	5.85	79.85	22.78
19	3.500	0.500	0.1100	5.72	17.43	78.57	4.77	83.34	24.20
20	3.500	0.500	0.1100	5.02	19.46	84.28	4.45	88.73	21.08

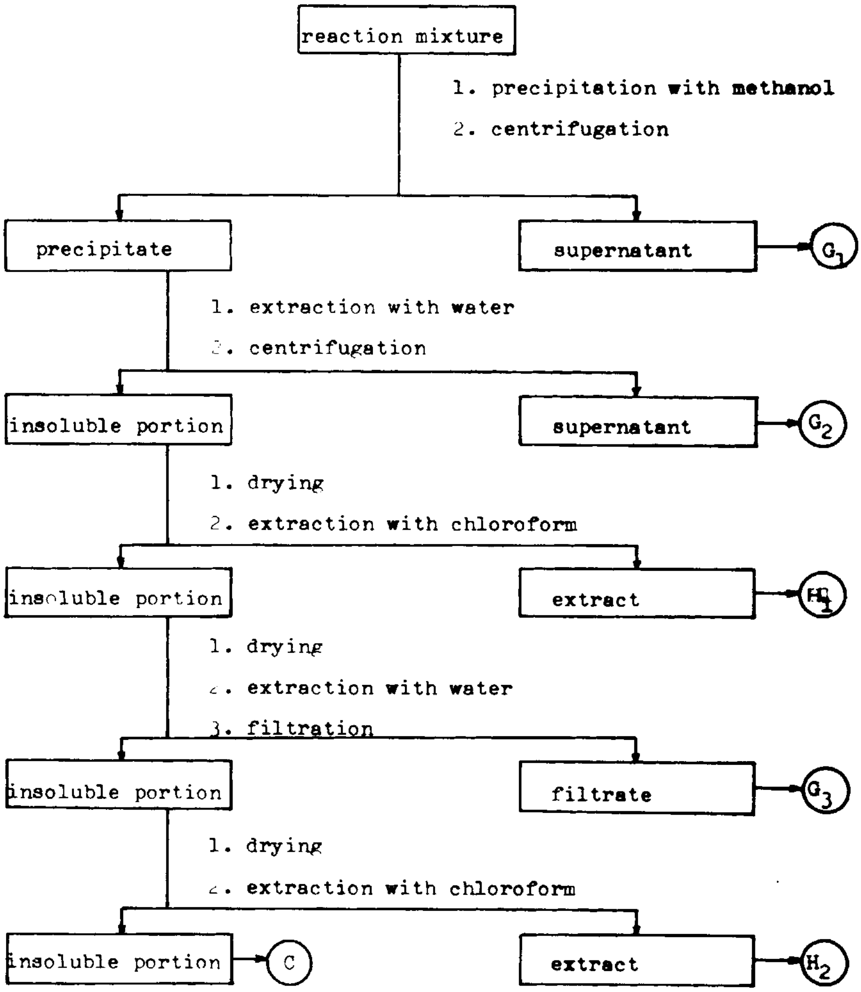

Fig. 1. Scheme of reaction mixture separation after MMA grafting onto gelatin.

$$y_4 = \frac{C - (G_0 - G)}{x_1} \times 100\,(\%) \tag{4}$$

$$y_5 = y_3 + y_4\,(\%) \tag{5}$$

$$y_6 = \frac{C - (G_0 - G)}{C} \times 100\,(\%) \tag{6}$$

where H = concentration of homopolymer of MMA (= $H_1 + H_2$; see Fig. 1), G = concentration of unreacted gelatin (= $G_1 + G_2 + G_3$; see Fig. 1), G_0 = initial concentration of gelatin, and C = copolymer concentration in the reaction mixture.

RESULTS AND DISCUSSION

To determine the influence of reaction conditions on the course of MMA grafting to gelatin, we have used the method of statistical planning of experiment.[16,17] Three factors have been observed, i.e., the concentration of MMA (x_1), $K_2S_2O_8$ (x_2), and $NaHSO_3$ (x_3) in the reaction mixture. Other factors, such as concentration of gelatin and temperature, are of little importance and have been chosen as constant. For describing the dependences of the values y_i characterizing the course of the reaction, we have used as a mathematical mode the second degree polynomial in the form

$$y_i = b_0 + b_1\tilde{x}_1 + b_2\tilde{x}_2 + b_3\tilde{x}_3 + b_{11}\tilde{x}_1^2 + b_{22}\tilde{x}_2^2 + b_{33}\tilde{x}_3^2 + b_{12}\tilde{x}_1\tilde{x}_2 + b_{13}\tilde{x}_1\tilde{x}_3 + b_{23}\tilde{x}_2\tilde{x}_3 \quad (7)$$

where the values $\tilde{x}_i$ are the coded values of the independent variables x_i. The conversion of $\tilde{x}_i$ to x_i is indicated in Table II. The ranges of the changes of independent variables have been determined according to the preliminary experiments.[15]

As dependent variables there have been observed efficiency of grafting (y_1), the conversion of gelatin (y_2), the conversion of MMA (y_3–y_5), and the content of PMMA in copolymer (y_6). These values have been computed from the experimental data as per eqs. (1)–(6), and are quoted in Table I.

The computation of the regression coefficients of the equations of type (7) has been carried out using the computer Hewlett-Packard 2100 A; the survey of the computed coefficients of the regression equations and indexes of correlation for all dependent variables y_i is given in Table III.

The efficiency of grafting (y_1) is significantly influenced by all parameters x_i. The stationary point of this function is situated outside the experimental area (Table IV). Within the experimental area it is possible to attain the maximum of 30% of the grafting efficiency (Figs. 2 and 3), which is much less than we have found[14] when initiating the grafting with Ce(IV) ions. This difference corresponds to the different mechanisms of the initiation with Ce(IV) ions and with the redox system. In case of the initiation with the redox system the probability of the direct creation of macroradicals is very low and the grafting is effected probably due to the chain transfer. The influence of the concentration of MMA (x_1) upon y_1 shows an extreme (minimum) at x_1 of about 4–5 %; with the reduction of the MMA concentration the efficiency of grafting increases (Fig. 3). Due to the fact that the

TABLE II
Relation Between Original and Coded Independent Variables

Factor	$\tilde{x}_i$ level: −1.682	−1	0	1	1.682
x_1	1.00	2.013	3.50	4.986	6.00
x_2	0.10	0.262	0.50	0.738	0.90
x_3	0.02	0.0565	0.11	0.1635	0.20

TABLE III
Coefficients of Regression Equations Type (7)[a]

Regression coefficient	y_1	y_2	y_3	y_4	y_5	y_6
b_0	5.9903	19.1252	79.7621	4.9526	84.9666	23.6564
b_1	−3.0466	(1.2666)	−3.9010	−1.7141	−10.0114	2.4716
b_2	−4.0371	−2.0408	(0.6662)	−1.9082	−5.6384	−7.1930
b_3	−2.6991	−2.0589	2.8926	−3.9829	−5.4867	−4.1762
b_{11}	2.9502	−2.4253	(−2.3389)	2.4209	(−1.5029)	5.4228
b_{22}	(0.5065)	(−1.4651)	−6.5419	0.5042	−7.6226	3.6422
b_{33}	2.6584	(−1.3873)	(−1.1206)	3.0257	(0.3201)	6.0806
b_{12}	(0.5400)	(−1.5300)	−4.2550	3.2050	−8.5450	4.1600
b_{13}	0.9325	(−1.5200)	(1.7700)	−2.1375	−7.8625	4.6950
b_{23}	−2.4925	(−1.1875)	10.6175	−3.3425	(−0.2199)	(0.2875)
Index of correlation $I(\tilde{x},y)$	0.8352	0.8170	0.7083	0.9207	0.7775	0.7528

[a] Values in parentheses are, according to the absolute value of T criterion, statistically insignificant.

TABLE IV
Coordinates of Stationary Points of y_i Functions

Function	y_1	y_2	y_3	y_4	y_5	y_6
$\tilde{x}_{1(s)}$	3.0208	0.7614	−0.8590	1.4532	−0.7871	−1.1845
$\tilde{x}_{2(s)}$	−15.1008	−0.7552	−0.2908	−1.3921	0.0087	1.6338
$\tilde{x}_{3(s)}$	−7.1024	−0.8362	−0.7653	0.4025	−1.0666	0.7621
$y_{i(s)}$ (%)	41.45	21.24	80.23	4.23	91.59	14.73
Type of extreme	Minimax	Maximum	Minimax	Minimax	Minimax	Minimum

works concerning acrylate grafting on collagen substrates often discuss the influence of composition of the initiation system,[6-8] Figure 2 illustrates this influence at the constant concentration of MMA. The efficiency of grafting increases with decreasing concentration of persulfate, the influence of the concentration of bisulfite exhibits an extreme. At the constant molar ratio of sulfite to persulfate (MR), different efficiencies of grafting are being obtained, depending on the concentration of the initiation system. The same is illustrated in Figure 3, where the constant MR values represent parallels with the horizontal axis. The dependence of the efficiency of grafting on MR is, therefore, not simple and changes with the concentration of MMA in the mixture and with the total concentration of the initiation system. Figure 4 shows the discussed dependence at the constant concentration of MMA and the constant concentration of persulphate. This dependence exhibits an extreme at MR of about 0.8–1.0 (according to the value x_2). When reducing MR under this value, the efficiency of grafting markedly increases. This means that the theoretical MR 0.5 [from eq. (8)] is not optimal.

$$H_2O + HSO_3^- + 2S_2O_8^{2-} \rightarrow 3HSO_4^- + 2SO_4^{\cdot -}$$
$$SO_4^{\cdot -} + H_2O \rightarrow HSO_4^- + HO^{\cdot} \qquad (8)$$

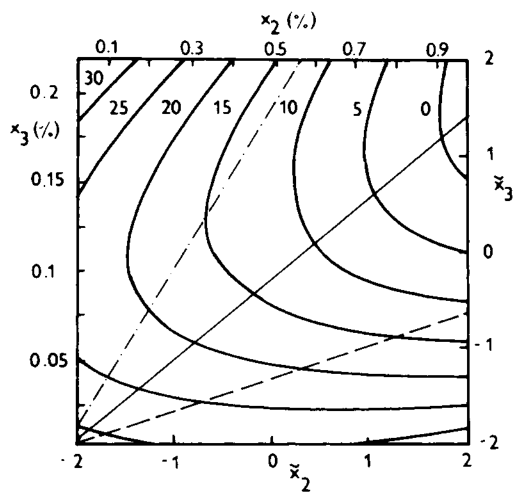

Fig. 2. Contour lines for grafting efficiency (y_1) as a function of persulfate (x_2) and bisulfite (x_3) concentrations, at constant MMA concentration 2%: (—) MR 0.2; (——) MR 0.5; (- · · · · -) MR 1.0.

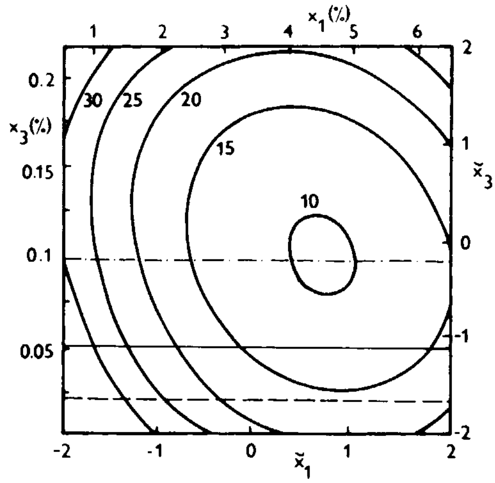

Fig. 3. Contour lines for grafting efficiency (y_1) as a function of MMA (x_1) and bisulfite (x_3) concentrations, at constant persulfate concentration 0.26%: (- - -) MR 0.2; (——) MR 0.5; (- · · · · -) MR 1.0.

The increase of the efficiency of grafting with the decreased MR has been observed only up to the value MR of about 0.2 (margin of the experiment). Logically it is possible to suppose that behind this value a decrease should occur due to the fact that the efficiency of the grafting cannot increase with decreased MR (and therefore also the decreased concentration of bisulfite) up to zero. This assumption is in good accordance with the results of some works[6–8] in which (naturally when grafting onto insoluble collagen) the optimum MR of about 0.2 has been found. We suppose in accordance with the results of Refs. 6 and 8 that the bisulfite concentration decrease (under the constant concentration of persulfate) below the stoichiometric MR results in lowering the primary radicals concentration, which reduces the probability of their recombination. The probability of forming relatively stable and immobile collageneous macroradicals on which the MMA grafts grow rises and the grafting efficiency increases. In the opposite case (i.e., with the bisulfite concentration increase which results also in the MR increase above the stoichiometric ratio) the concentration of formeed primary radicals remains constant. However, the excess of bisulfite as a strong reducing agent may cause their reduction to anions, e.g., by the eq. (9) or there may arise an adduct with another transfer constants:

$$2SO_4^{\cdot -} + HSO_3^- \rightarrow 2\,HSO_4^- + SO_4^{2-} + H^+$$
$$\text{or } 2HO^{\cdot} + HSO_3^- \rightarrow SO_4^{2-} + H_2O + H^+ \qquad (9)$$

As a result, the concentration of free primary radicals falls down, and the grafting efficiency increases. Figure 4 shows well the negative influence of the increase of the whole concentration of the initiation system (which increases in this case with the increased persulfate concentration) on the efficiency of grafting; at MR 0.2 this negative influence is low but increases rapidly with increasing MR. The negative influence of increased concen-

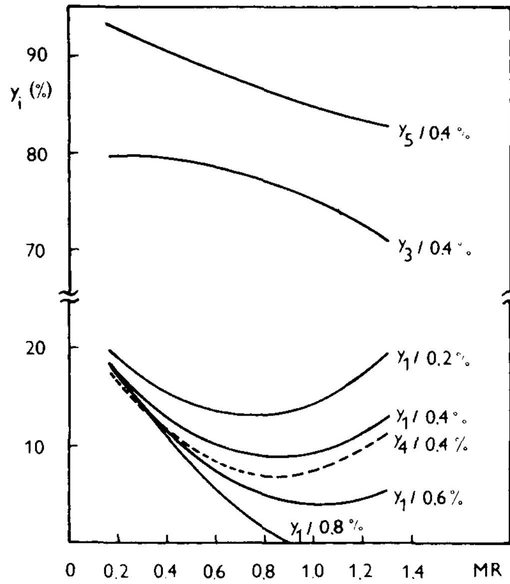

Fig. 4. The influence of MR values on dependent variables y_i at concentration of MMA 3.1% and at designated constant concentration of persulfate (y_i/% of $K_2S_2O_8$).

tration of the initiation system on the efficiency of grafting is in contradiction with the results of Smets and Herthage[18] and indicates that the creation of macroradicals is in the case negligible.

From the point of view of the utilization of the initial material the conversion of gelatin (y_2) is an important value. All parameters x_i have a statistically important influence on this value (Table III), the maximum of the function y_2 (Table IV) is situated in the experimental area. Its value (21.24%) is almost twice lower than in grafting initiated with Ce(IV) ions.[14]

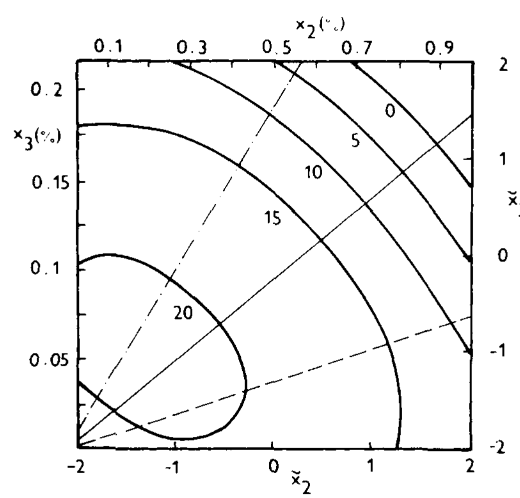

Fig. 5. Contour lines for gelatin conversion (y_2) as a function of persulfate (x_2) and bisulfite (x_3) concentrations, at constant MMA concentration 5%: (—) MR 0.2; (——) MR 0.5; (- - - - -) MR 1.0.

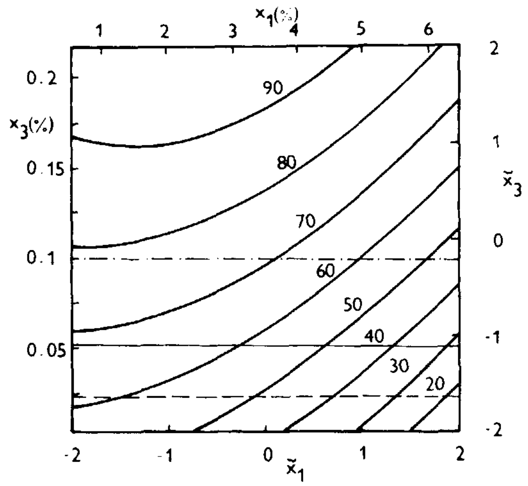

Fig. 6. Contour lines for MMA to homopolymer conversion (y_3) as a function of MMA (x_1) and bisulfite (x_3) concentrations, at constant persulfate concentration 0.74%: (—) MR 0.2; (— —) MR 0.5; (- · · · · -) MR 1.0.

The optimum concentration of MMA is about 4.6% (the mass ratio MMA/gelatin = 1.55); when increasing or decreasing it, the conversion decreases. Figure 5 shows that the degree of gelatin utilization depends only very little on the MR value, but it is very negatively influenced by increasing the concentration of the initiation system.

During the grafting a considerable fraction of homopolymer (PMMA) is being produced. The extent of homopolymerization (y_3) is significantly influenced by all independent variables (Table III). The influence of MMA concentration in the mixture on the PMMA production is greatly dependent on the concentration of the components in the initiation system; e.g., at the persulfate concentration above 0.5%, the increased concentration of mon-

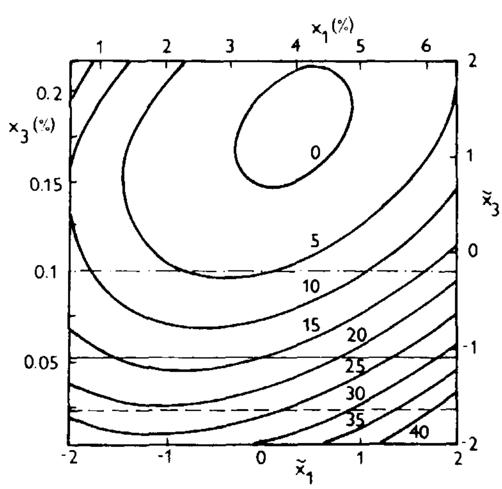

Fig. 7. Contour lines for MMA to copolymer conversion (y_4) as a function of MMA (x_1) and bisulfite (x_3) concentrations, at constant persulfate concentration 0.74%: (—) MR 0.2; (——) MR 0.5; (- · · · · -) MR 1.0.

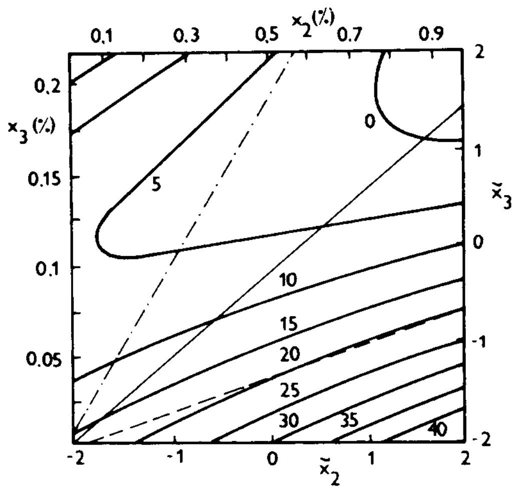

Fig. 8. Contour lines for MMA to copolymer conversion (y_4) as a function of persulfate (x_2) and bisulfite (x_3) concentrations, at constant MMA concentration 5%: (—) MR 0.2; (——) MR 0.5; (- - - - -) MR 1.0.

omer leads to a lower formation of PMMA up to the value less than 30% (Fig. 6). The concentration of persulfate below 0.3% yields extreme content of the homopolymer at MMA concentration 3.5%. Favorable influence on the limitation of homopolymerization exhibits the decreasing MR value (Fig. 4), a sign of the optimum being observed at MR 0.2.

The conversion of MMA to copolymer (y_4) significantly depends on all factors x_i (Table III) and, in experimental area, it attains the maximum value of about 35%. The dependence of y_4 on the concentrations of MMA and bisulfite is shown in Figure 7. At the MMA concentration higher than 5%, the conversion higher than 30% can be obtained. The dependence of y_4 on the composition of the initiation system at the constant value of the MMA concentration is demonstrated in Figures 4 and 8. Obviously, it is necessary to reduce the MR value below 0.2, for attaining a high overall copolymer content.

The overall conversion of MMA (y_5) is an important value for the utilization of MMA and also for the security of work (toxicity of MMA). This function is characterized by a minimax, the coordinates of which are given in Table IV. The influence of the concentration of all reaction components is statistically relevant (Table III). In the experimental area it is possible to attain a 100% MMA conversion at the MMA concentration above 5% (Fig. 9) and at the lowest possible concentration of the initiation system (Fig. 10). The optimum concentration of persulfate is about 0.3% (Fig. 10); the influence of the bisulfite concentration depends on the MMA concentration. The decreasing of the MR value has a favorable influence on the MMA conversion, supposing that MMA concentration is higher than 3% (Figs. 4 and 9).

The last investigated dependent variable is the PMMA content in copolymer (y_6), which influences the characteristics of the product and the possibility of its utilization. Owing to the fact that there is no verification of the characteristics of the grafting product in this work, it is not possible

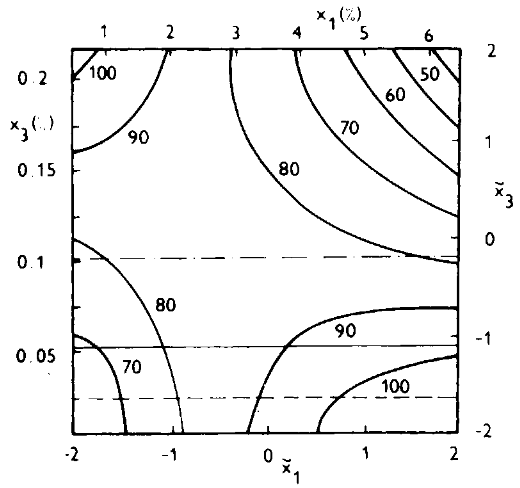

Fig. 9. Contour lines for total MMA conversion (y_5) as a function of MMA (x_1) and bisulfite (x_3) concentrations, at constant persulfate concentration 0.26%: (- - -) MR 0.2; (——) 0.5; (- · · · · -) MR 1.0.

to determine the optimum value of y_6. In practical application of the product, the value y_6 will be probably one of the most important factors.

Since it is not possible to derive all influences of the composition of reaction system on the course of grafting from the quoted figures, these are summarized according to the global analysis in Table V. It is obvious that the influence of reaction conditions is very complex, and it is not possible to evaluate in a simple way the influence of one factor without taking into consideration the values of other factors. The modification of the reaction conditions for attaining an optimum for all dependent variables is not possible, and it is necessary to choose a compromising solution. In

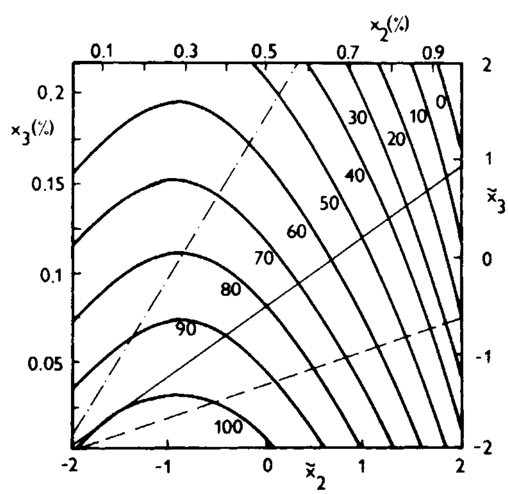

Fig. 10. Contour lines for total MMA conversion (y_5) as a function of persulfate (x_2) and bisulfite (x_3) concentrations, at MMA concentration 5%: (—) MR 0.2; (——) MR 0.5; (- · · · · -) MR 1.0.

TABLE V
Some Orientative Influences of Reaction Mixture Composition on Dependent Variables y_i

		Change of the value y_i with increasing values of		
y_i	Meaning of y_i	x_1 (% MMA)	MR ($NaHSO_3$/ $K_2S_2O_8$)	Concentration of initiation system (at MR = const)
y_1	Grafting efficiency	Decreasing up to $x_1 = 4.5\%$, then increasing	At MR < 1 decreasing, at MR > 1 increasing	Decreasing in the whole extent
y_2	Conversion of gelatin	Increasing up to $x_1 = 4.5\%$, then decreasing	Slightly increasing at MR < 0.5, at MR > 0.5 decreasing, at $x_1 > 5\%$ independent	Decreasign in the whole extent at $x_1 > 5\%$, at $x_1 < 5\%$ the maximum in the zone 0.4–0.5% x_2
y_3	Conversion of MMA to homopolymer	At $x_2 < 0.25\%$ maximum at $x_1 = 3\%$ up to 4%, at $x_2 > 0.25\%$ decreasing	At $x_2 < 0.25\%$ decreasing, at $x_2 > 0.25\%$ increasing when supposing MR < 0.8	At 0.5 < MR < 1 independent, at MR < 0.5 and MR > 1 decreasing
y_4	Conversion of MMA to copolymer	Slightly decreasing up to $x_1 = 2$–3%, at $x_1 > 5\%$ quickly increasing	Markedly decreasing in the whole extent (condition MR < 1)	At MR < 1 decreasing, with the decreasing MR the influence weakens, at MR-0.2 without influence
y_5	Total conversion of MMA	At $x_2 < 0.7\%$ increasing when supposing $x_3 < 0.1\%$, at x_2 above 0.7% decreasing	At $x_1 > 2\%$, $x_2 < 0.5\%$, and MR $\leq$ 1 decreasing, when increasing x_2 above 0.5% the influence is inverse	At $x_1 > 4\%$ considerably decreasing in the whole extent independently on MR
y_6	pMMA content in copolymer	Markedly decreasing up to $x_1 = 4\%$, slightly increasing at $x_1 > 4\%$	Decreasing in the whole extent (condition MR $\leq$ 1)	Markedly decreasing in the whole extent independently on MR

our case the optimum value x_1 for the majority of the dependent variables is about 4–5%. In Figure 11 there are, therefore, plotted the zones of extremely attainable values y_i at the constant 5% MMA concentration. The figure shows that there is no coincidence of all zones, and it is therefore necessary to choose the dominant dependent variable. If we want to have a 100% MMA conversion, we get a grafting efficiency of about 15%; the extent of gelatin utilization will be about 20%, but the extent of homopolymerization will be higher than 75%. If we try to reduce the extent of homopolymerization and to get a higher conversion of MMA to copolymer, we must take into account the reduction of utilization of the gelatin and a part of nonreacted MMA will remain in the mixture. The choice of conditions will depend also on the required content of PMMA in the copolymer as it has been discussed above.

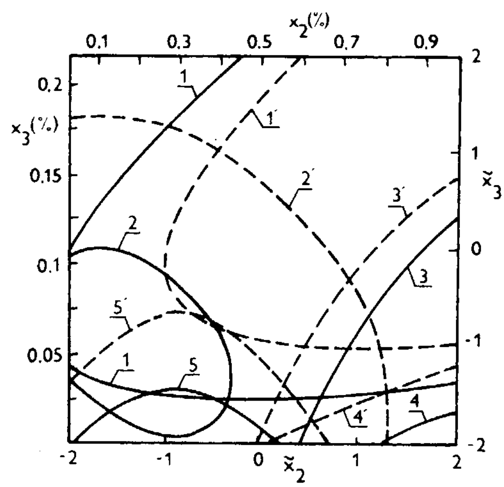

Fig. 11. Contour lines of optimum values of dependent variables y_i as a function of persulfate (x_2) and bisulfite (x_3) concentrations, at MMA concentration 5%: (1 – y_1 = 15%, 1' – y_1 = 10%, 2 – y_2 = 20%, 2' – y_2 = 15%, 3 – y_3 = 50%, 3' – y_3 = 60%, 4 – y_4 = 40%, 4' – y_4 = 30%, 5 – y_5 = 100%, 5' – y_5 = 90%).

CONCLUSION

The influence of reaction conditions on grafting of MMA onto gelatin initiated by bisulfite–persulfate redox system has been studied. The statistical analysis of the obtained results shows that the grafting process is significantly influenced by the concentration of monomer in the mixture and by the composition of the redox system. In comparison with the grafting initiated by Ce(IV) ions,[14] there is a considerable reduction of the grafting efficiency, and also the area of the total MMA conversion is much smaller. There is an advantage in working in a neutral medium and in the fact that no ions of heavy metals are admixed into the product. In contradiction to the formerly published papers, no optimal molar ratio of bisulfite/persulfate has been found, but it is taken for granted that the majority of the studied parameters improve with the decreasing of this molar ratio below the theoretical value 0.5 up to the value 0.2 and also with the decreased concentration of both components of the initiation system. The influence of changes in the composition of the reaction system on the variables characterizing the course of grafting is qualitatively evaluated in Table V. It is evident that we cannot choose such reaction conditions which would lead to the results situated near to the optimal values of all depended variables. It is, therefore, necessary to choose the required values of one or two dependent variables; the values of other dependent variables are then inferior. The most important dependent variable from the point of view of the practical utilization of the grafting products will probably be the composition of the grafted product. The influence of the product composition on its characteristics has not been studied.

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