

# **Fe<sup>2+</sup>-Thioureadioxide-H<sub>2</sub>O<sub>2</sub>-Induced Polymerization of Glycidyl Methacrylate and Its Mixtures with Acrylamide, Acrylonitrile, Butylmethacrylate, or Styrene with Cotton Fabric**

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## **Synopsis**

Fe<sup>2+</sup>-thioureadioxide-H<sub>2</sub>O<sub>2</sub>-induced polymerization of glycidyl methacrylate (GMA) and its mixtures with acrylamide (Aam), acrylonitrile (AN), butylmethacrylate (BMA), or styrene was investigated at different temperatures (50–95°C), for different periods of time (5–130 min) using different concentrations of Fe<sup>2+</sup>, thioureadioxide, and H<sub>2</sub>O<sub>2</sub>. The add-on increased by increasing the thioureadioxide concentration up to 0.05% then decreased. H<sub>2</sub>O<sub>2</sub> concentration of 0.005% constituted the optimal for GMA and GMA/Aam mixtures, and 0.02% H<sub>2</sub>O<sub>2</sub> for GMA/AN, GMA/BMA and GMA/styrene mixtures. Increasing the concentration of GMA either alone or in admixtures resulted in improved add-ons; the magnitude of this improvement relied on the nature of the monomer used along with GMA. The polymerization reaction was characterized by an initial fast rate followed by a slower one irrespective of monomer or monomer mixtures used. Presence of Aam along with GMA offset the fast termination observed with the latter at higher temperatures (above 60°C). GMA/Aam mixtures produced higher add-ons than Aam alone irrespective of their ratios in the mixtures, indicating activation of Aam with GMA. On the other hand, Aam deactivated GMA. Similar situation was encountered when styrene or acrylonitrile was used instead of Aam except that the percent add-ons obtained with GMA/AN mixtures decreased upon raising the polymerization temperature above 80°C. Contribution of GMA in the add-ons obtained with the different mixtures was also examined. For instance, the add-on was composed mainly of poly(GMA) when GMA/Aam at a ratio of 8:2 was used. On the other hand, using GMA/Aam at a ratio of 2:8 brought about add-ons of poly(GMA/Aam) in which the concentration of GMA and Aam were roughly equal.

## **INTRODUCTION**

Free-radical polymerization reactions of vinyl monomers with cellulose and modified celluloses most probably involve grafting.<sup>1</sup> Polymerization of acrylamide,<sup>2–9</sup> acrylonitrile,<sup>2,8,9,10–15</sup> butylmethacrylate,<sup>16</sup> styrene,<sup>17–20</sup> and glycidyl methacrylate<sup>21–24</sup> with cotton cellulose using physical and chemical means for initiation has been reported. Polymerization of binary mixtures of some vinyl mixtures with celluloses has also been reported.<sup>9,25–30</sup> However, to the authors' knowledge, no work has yet been published on polymerization of cotton cellulose with binary mixtures containing glycidyl methacrylate together with acrylamide, acrylonitrile, butylmethacrylate, or styrene using Fe<sup>2+</sup>-thioureadioxide-H<sub>2</sub>O<sub>2</sub> redox system as initiator. Recent studies<sup>31</sup> have disclosed that Fe<sup>2+</sup>-thioureadioxide-H<sub>2</sub>O<sub>2</sub> form a more effective redox-initiating system than do Fe<sup>2+</sup>-H<sub>2</sub>O<sub>2</sub> and thioureadioxide-H<sub>2</sub>O<sub>2</sub> systems.

The present work is undertaken with a view of studying (a) factors affecting the percent polymer add-on when cotton fabric is polymerized with glycidyl

methacrylate alone or together with acrylamide, acrylonitrile, butylmethacrylate, or styrene and (b) the contribution of the glycidyl methacrylate in the add-on.

## EXPERIMENTAL

Mill-desized, kier-boiled, and bleached cotton fabric (140 g/m<sup>2</sup>) was kindly supplied by Misr El-Bieda Co., Kafr El-Dawar. The fabric was further purified by treating it with a 20 g/L sodium carbonate solution, followed by washing well and drying at ambient conditions.

Glycidyl methacrylate (GMA) obtained from a commercial source was freshly distilled and the fraction of 98°C/11 mmHg was used. Acrylonitrile (AN), butylmethacrylate (BMA), and styrene (AR chemicals) were freshly distilled before use. Acrylamide (Aam) was of AR grade chemicals.

### Polymerization Procedure

Unless otherwise stated, the sample of cotton fabric was first impregnated in freshly prepared aqueous ferrous ammonium sulphate (0.025%) for 15 min at 25°C using a material to liquor ratio of 1:50. The sample was then squeezed, washed thoroughly with distilled water, and dried. Chemical analysis<sup>32</sup> showed that the sample contains 0.031% Fe<sup>2+</sup>.

Accurate weight of the Fe<sup>2+</sup>-containing sample was immersed in an aqueous solution containing the monomer or the monomer mixture, H<sub>2</sub>O<sub>2</sub>, thiourea-dioxide, and an emulsifying agent (Emulphur P, BASF) using a material-to-liquor ratio of 1:30. The reaction was then allowed to proceed while stirring at the specific temperature for the desired duration. Details of the conditions used are given in the text. Fabric samples containing poly(GMA) were subjected to repeated soxhlet extraction with ethyl methyl ketone (EMK). Further soxhlet extraction with dimethylformamide, benzene, and ethyl acetate was carried out in cases of samples polymerized with GMA/AN, GMA/styrene, and GMA/BMA mixtures, respectively. In case of samples polymerized with the GMA/Aam mixture, EMK soxhlet extraction was followed by repeated washing in boiling water. In all cases, the soxhlet extraction and/or boiling in water were continued till constant weight.

The percent polymer add-on was calculated as follows:

$$\left( \begin{array}{l} \text{polymer} \\ \text{add-on \%} \end{array} \right) = \frac{(\text{wt of polymerized fabric}) - (\text{wt of original fabric})}{\text{wt of original fabric}} \times 100$$

### Analysis

#### *Nitrogen Content*

Nitrogen content of the grafted fabric was determined by making use of the Kjeldahl method.<sup>33</sup>

### Free Epoxy-Ring

For estimation of free epoxy-rings in poly(GMA)-containing cotton, the following procedure was adopted, which, in essence, is based on methods described elsewhere<sup>34,35</sup>. Fabric sample (ca. 1 g) was immersed in concn HCl:dioxane mixture (3:1) at room temperature for 2 h using a material-to-liquor ratio of 1:10. The sample was then thoroughly washed with distilled water to avoid any traces of the acid. Accurate weight of the acid-free sample (20–25 mg) was combusted in an Erlenmayer flask containing 1–2 mL of 0.5 N KOH, 15 mL 6% H<sub>2</sub>O<sub>2</sub>, and filled with O<sub>2</sub>. The flask was then allowed to cool at room temperature under shaking. After washing, the glass stopper and the platinum wire with the least amount of bidistilled water, the solution was boiled for 5 min to decompose excess H<sub>2</sub>O<sub>2</sub>. The solution was allowed to cool; then 80 mL of ethanol was added. Five drops of alcoholic bromophenol blue solution (0.05%) were added and the whole solution neutralized with 0.5 N HNO<sub>3</sub> till the end point of the indicator. 1 mL of 0.5 N HNO<sub>3</sub> was also added to bring the pH to a value of about 3.5. At this end 15 drops of alcoholic diphenylcarbazone (0.5%) were added and then titrated against 0.01 N Hg(NO<sub>3</sub>)<sub>2</sub> till the end point (from faint yellow to cherry red). The percent polymer add-on of poly(glycidyl-methacrylate)-rest was calculated as follows:

$$\text{polymer add-on \%} = \frac{(V - V_1) \cdot N \cdot 0.1785 \cdot 100}{G}$$

where  $V$  and  $V_1$  = volume (mL) of 0.01 N Hg(NO<sub>3</sub>)<sub>2</sub> of solution and blank, respectively;  $N$  = normality of Hg(NO<sub>3</sub>)<sub>2</sub> used; and  $G$  = weight of sample (g).

## RESULTS AND DISCUSSION

### Polymerization Temperature

Figure 1 shows the effect of temperature on polymerization of GMA and Aam as well as their mixtures with cotton cellulose on the percent add-on. It is seen that below 50°C, the GMA/Aam mixture could not be polymerized with cotton. On the other hand, the percent add-ons obtained with these monomer mixtures increase by raising the polymerization temperature from 50°C to 60°C irrespective of the ratio of GMA to Aam in the mixtures. Further increase in the polymerization temperature has practically no effect on the percent add-ons. The same situation is encountered when Aam was used alone. With GMA, on the other hand, the percent add-on decreases as the polymerization temperature is raised from 50°C to 95°C. If this is attributed to the fast rate of termination as the temperature increases,<sup>36</sup> current data suggest that the presence of Aam during polymerization of GMA with cotton cellulose offsets the fast termination rate. Furthermore, the higher add-ons observed with GMA/Aam mixtures, regardless of their ratio in the polymerization system, than those of Aam indicate that GMA activates Aam. Meanwhile, Aam deactivates GMA since the add-ons observed with the latter are significantly higher than those for GMA/Aam mixtures. Possible addition of the amide groups of Aam to the epoxide groups of GMA may account for this deactivation.

Figure 2 shows that polymerization of GMA/styrene with cotton cellulose results in considerable increments in the weight of cotton (add-ons) provided

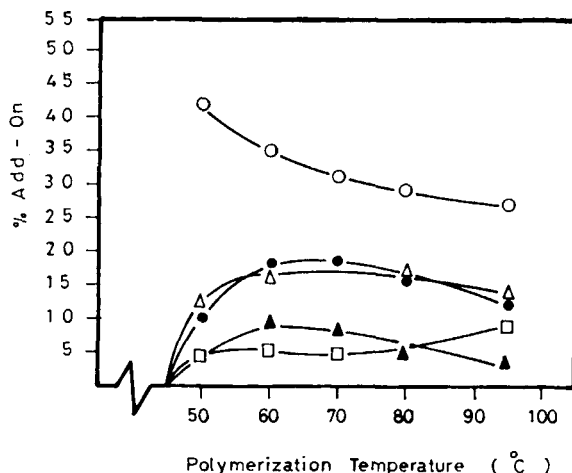


Fig. 1. Effect of polymerization temperature on % polymer add-on.  $[H_2O_2]$ , 0.025%; [thioureadioxide], 0.033%;  $[Fe^{2+}]$ , 0.031%; [monomer or monomer mixtures], 50% based on weight of fabric; 4 drops of Emalpur P; reaction time = 60 min; material-to-liquor ratio, 1:30. (○) GMA; (●) GMA/Aam (8:2); (△) GMA/Aam (5:5); (▲) GMA/Aam (2:8); (□) Aam.

that the polymerization temperature is above 50°C. Raising the temperature to 60°C is accompanied by a significant enhancement in percent add-ons when mixtures of GMA/styrene at ratios of 8:2 and 5:5 were used. A further increase in temperature has no significant effect on the percent add-ons obtained with these mixtures. With mixtures of GMA/styrene at a ratio of 2:8, the add-on increases by increasing the polymerization temperature from 50°C to 95°C. This is rather the trend observed when styrene alone was polymerized with cotton cellulose. It is also seen that GMA activates styrene since mixtures of GMA/styrene bring about higher add-ons than styrene alone. On the contrary, styrene deactivates GMA because the add-ons obtained with the latter are significantly higher than those of GMA/styrene mixtures. However, the presence of styrene

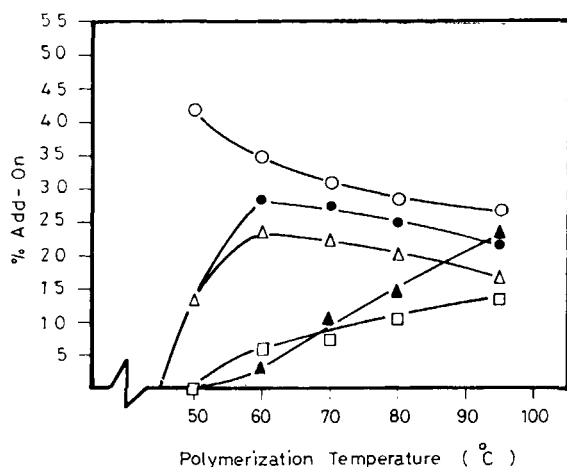


Fig. 2. Variation of the polymer add-on with polymerization temperature. Conditions as in Figure 1. (○) GMA; (●) GMA/styrene (8:2); (△) GMA/styrene (5:5); (▲) GMA/styrene (2:8); (□) styrene.

during polymerization of GMA with cotton prevents the decrease in the add-ons as the polymerization temperature increases, similar to Aam.

Figure 3 shows the effect of temperature on polymerization of GMA and AN as well as their mixtures with cotton cellulose on the percent add-on. It is clear that GMA/AN mixtures show trends similar to those found with GMA/Aam mixtures except that the percent add-ons tend to decrease when the temperature is raised beyond 80°C. This is rather a direct consequence of the fact that the add-ons of AN tend also to decrease at polymerization temperatures higher than 80°C.

Figure 4 shows the effect of polymerization temperature on percent add-on on cotton cellulose when GMA, BMA, and their mixtures were polymerized with cotton. It is seen that the add-on obtained with BMA increases by increasing

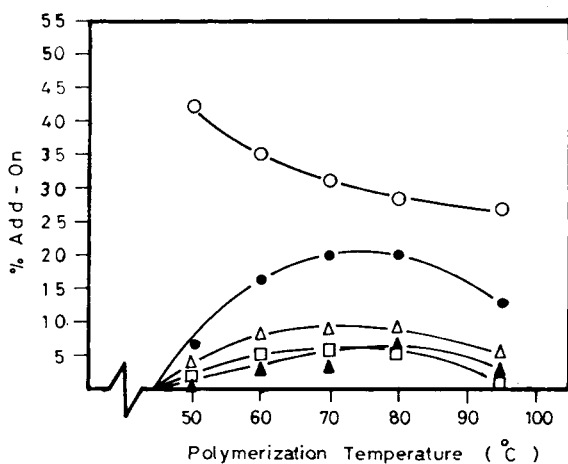


Fig. 3. Polymer add-on vs. polymerization temperature. Conditions as in Figure 1. (○) GMA; (●) GMA/AN (8:2); (△) GMA/AN (5:5); (▲) GMA/AN (2:8); (□) NA.

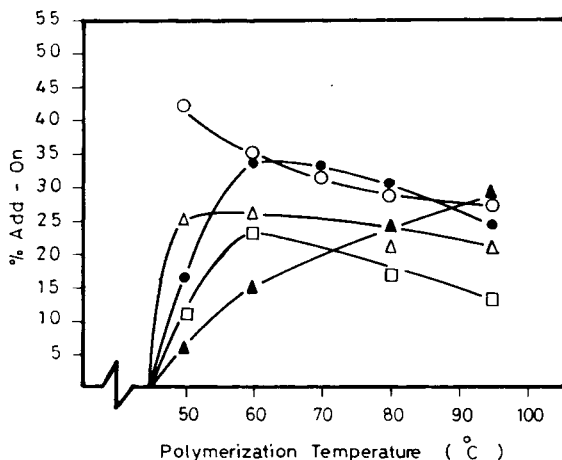


Fig. 4. Polymer add-on as a function of polymerization temperature. Conditions as in Figure 1. (○) GMA; (●) GMA/BMA (8:2); (△) GMA/BMA (5:5); (▲) GMA/BMA (2:8); (□) BMA.

the polymerization temperature from 50°C to 60°C. A further increase in temperature up to 95°C is accompanied by a decrease in the add-on, most probably due to the fast rate of termination at higher temperature. A similar trend is observed with GMA/BMA mixture at ratios of 8:2 and 5:5. On the other hand, with the GMA/BMA mixture at a ratio of 2:8 the add-on increases as the polymerization temperature increases within the range studied, indicating that the presence of BMA at a higher ratio together with GMA offsets the fast termination rate found with GMA.

### Hydrogen Peroxide Concentration

Figure 5 shows the percent add-on as a function of  $H_2O_2$  concentration when GMA and its mixture with Aam, AN, styrene, and BMA at a ratio of 8:2 were polymerized with cotton cellulose in the presence of thiourea dioxide (0.033%) and  $Fe^{2+}$  (0.031%) at 60°C for 60 min using a material-to-liquor ratio of 1:30. The results reveal: (a) that, with the exception of the GMA/styrene mixture, polymerization of GMA either alone or as mixtures does occur in the absence of  $H_2O_2$ ; (b) that the percent add-on obtained with GMA and its mixtures in absence of  $H_2O_2$  depends upon the nature of the second monomer, in the order

GMA > GMA/AN > GMA/BMA > GMA/Aam > GMA/styrene

(c) that inclusion of  $H_2O_2$  in the polymerization system enhances the percent add-on considerably irrespective of the monomer used; (d) that there is an optimal  $H_2O_2$  concentration at which a maximum percent polymer add-on could

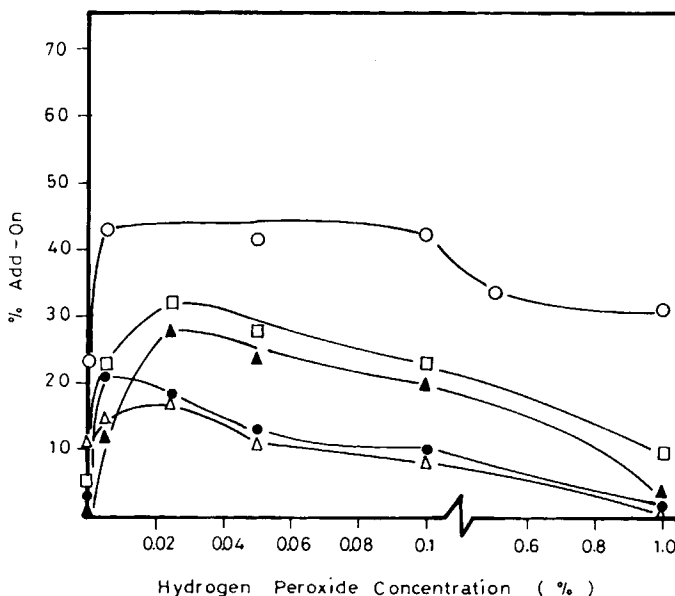
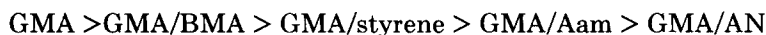
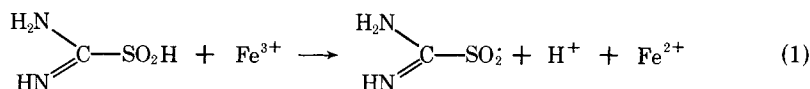


Fig. 5. Effect of  $H_2O_2$  concentration on % polymer add-on. [Thiourea dioxide], 0.033%; [ $Fe^{2+}$ ], 0.031%; [monomer or monomer mixtures], 50% based on weight of fabric; 4 drops Emalpur P; reaction time = 60 min; reaction temperature = 60°C; material-to-liquor ratio, 1:30. (○) GMA; (●) GMA/Aam (8:2); (△) GMA/AN (8:2); (▲) GMA/Styrene (8:2); (□) GMA/BMA (8:2).

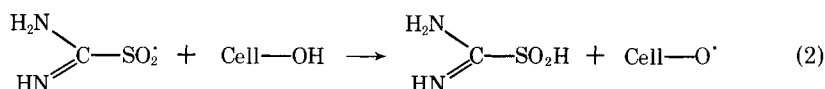
be achieved; (e) that the optimal H<sub>2</sub>O<sub>2</sub> concentrations amount to 0.005% for GMA and GMA/Aam mixtures and 0.02% for GMA/BMA, GMA/AN, and GMA/styrene mixtures; and (f) that the add-ons obtained at the optimal H<sub>2</sub>O<sub>2</sub> follow the order



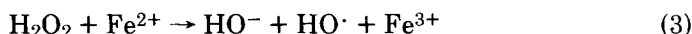
The occurrence of polymerization of GMA, alone and in admixture with other monomers, in the absence of H<sub>2</sub>O<sub>2</sub>, i.e. under the influence of Fe<sup>2+</sup> ion and thioureadioxide, would indicate that Fe<sup>2+</sup> ion is oxidized to Fe<sup>3+</sup> ion by atmospheric oxygen. The Fe<sup>3+</sup> ion so formed reacts with thioureadioxide to produce a free-radical intermediate as shown in the reaction suggested by



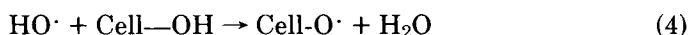
The reaction of the HN=C(NH<sub>2</sub>)—SO<sub>2</sub> radical with cellulose (Cell—OH) results in a cellulose macroradical and thioureadioxide as represented by



In the presence of H<sub>2</sub>O<sub>2</sub>, other free radical species, i.e., HO<sup>·</sup> radicals, would be formed according to the reaction suggested by



The reaction of the HO<sup>·</sup> radical with cellulose gives rise to cellulose macroradical as represented by



Hence, the higher add-on observed in the presence of H<sub>2</sub>O<sub>2</sub> at the optimal concentration suggests that cellulose macroradicals formed according to reactions (2) and (4) are in essence captured by the monomer or monomer mixtures leading to polymerization with cotton cellulose. Using H<sub>2</sub>O<sub>2</sub> at concentrations higher than those of the optimal results in the abundance of HO<sup>·</sup> radicals which may participate in termination of cellulose macroradicals, the reaction with Fe<sup>2+</sup> ion and thioureadioxide radicals thereby leading to lower add-ons.<sup>31</sup>

### Thioureadioxide Concentration

Figure 6 shows variation of percent add-on with thioureadioxide concentration when GMA and its mixtures with Aam, AN, styrene, and BMA at a ratio of 8:2 were polymerized with cotton cellulose in the presence of H<sub>2</sub>O<sub>2</sub> (0.025%) and Fe<sup>2+</sup> (0.031%) at 60°C for 60 min, using a material-to-liquor ratio of 1:30. It is obvious that, in the absence of thioureadioxide, the add-on is either quite poor, as in cases of GMA/BMA and GMA/Aam mixtures, or nil, as in cases of GMA and GMA/styrene and GMA/AN mixtures. In the presence of thioureadioxide, on the other hand, the add-on is quite significant irrespective of the monomer used. However, the magnitude of the add-on is determined by the thioureadioxide concentration.

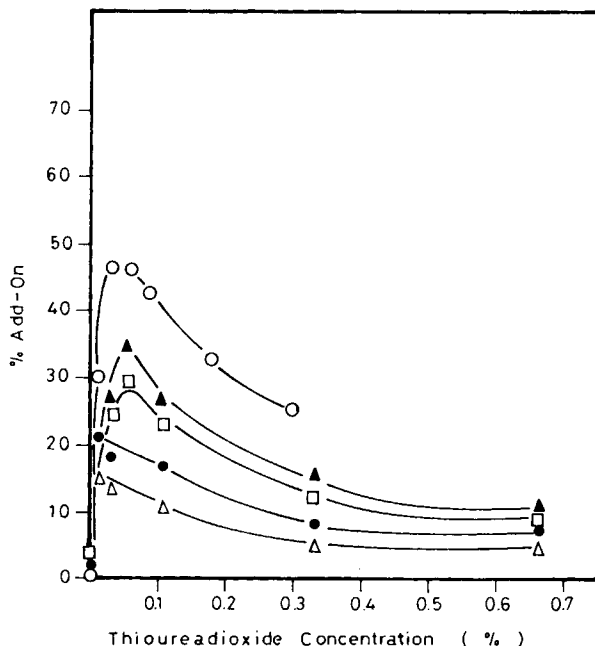


Fig. 6. Effect of thiourea dioxide concentration on % polymer add-on.  $[H_2O_2]$ , 0.025%;  $[Fe^{2+}]$ , 0.031%; [monomer or monomer mixtures], 50% based on weight of fabric; 4 drops Emalpur P; reaction time = 60 min; reaction temperature = 60°C; material-to-liquor ratio, 1:30. (O) GMA; (●) GMA/Aam (8:2); (Δ) GMA/AN (8:2); (▲) GMA/Styrene (8:2); (□) GMA/BMA (8:2).

Generally the add-on increases as the thiourea dioxide increases up to 0.05% and then decreases upon further increase in the thiourea dioxide concentration. This suggests that thiourea dioxide performs two functions: (a) participation in initiation of vinyl polymerization with cotton cellulose and (b) participation in termination of cellulose macroradicals, primary free radicals, and growing chain radicals. It is likely that thiourea dioxide up to a concentration of 0.05% is involved essentially in free radical initiation whereas at higher concentrations it acts mainly as a radical scavenger.

### Monomer Concentration

Figure 7 shows the effect of the concentration of GMA and its mixtures with Aam, AN, styrene, and BMA at a ratio of 2:8 on the percent add-on when they were polymerized with cotton in presence of  $H_2O_2$  (0.025%),  $Fe^{2+}$  (0.031%), and thiourea dioxide (0.033%) at 60°C for 60 min, using a material-to-liquor ratio of 1:30. It is seen that increasing the concentration of GMA alone or in admixtures with the said monomers is accompanied by a significant enhancement in the percent add-on. However, the magnitude of the latter depends upon the nature of the monomer used along with GMA. Of the mixtures used, the GMA/BMA mixture shows the highest percent add-on while GMA/AN shows the least. Furthermore, none of the mixtures could bring about an add-on which could be compared with those of GMA, irrespective of the concentration used. The add-ons obtained with GMA at different concentrations are significantly higher



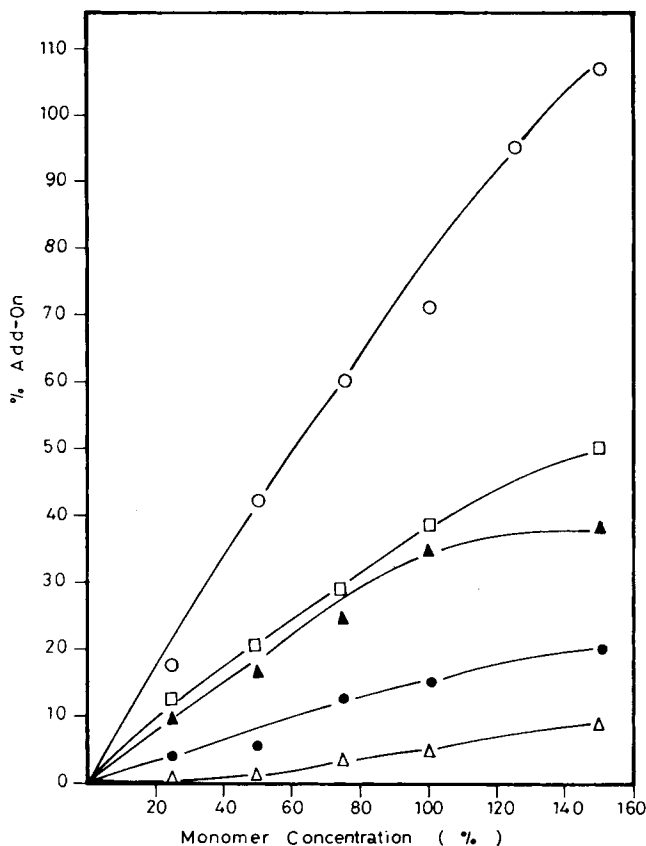


Fig. 7. Effect of monomer or monomer mixtures concentration (based on the weight of fabric) on % polymer add-on. [H<sub>2</sub>O<sub>2</sub>], 0.025%; [thioureadioxide], 0.033%; [Fe<sup>2+</sup>], 0.031%; reaction time = 60 min; reaction temperature = 60°C; material-to-liquor ratio, 1:30. (○) GMA; (●) GMA/Aam (2:8); (△) GMA/AN (2:8); (▲) GMA/Styrene (2:8); (□) GMA/BMA (2:8).

than their mates obtained with its mixture with the other monomers in question, indicating deactivation of GMA by these monomers under the conditions used.

### Time Of Polymerization

Figure 8 shows the effect of time of polymerization of GMA and its mixtures with Aam, AN, styrene, and BMA at a ratio of 8:2 on the percent add-on when they were polymerized with cotton cellulose using H<sub>2</sub>O<sub>2</sub> (0.025%), Fe<sup>2+</sup> (0.031%), and thioureadioxide (0.033%) at 60°C, using a material-to-liquor ratio of 1:30. It is apparent that the polymerization reaction is characterized by an initial fast rate followed by a slower rate regardless of the monomer or monomer mixtures used. However, the said monomers seem to activate GMA during the initial stages of the reaction since the add-ons obtained with the GMA mixtures are higher than those of GMA alone. Furthermore, this activation seems to be in full swing in the case of the GMA/Aam mixture and least in the case of the GMA/BMA mixtures. The opposite holds true for the later stages of the reaction

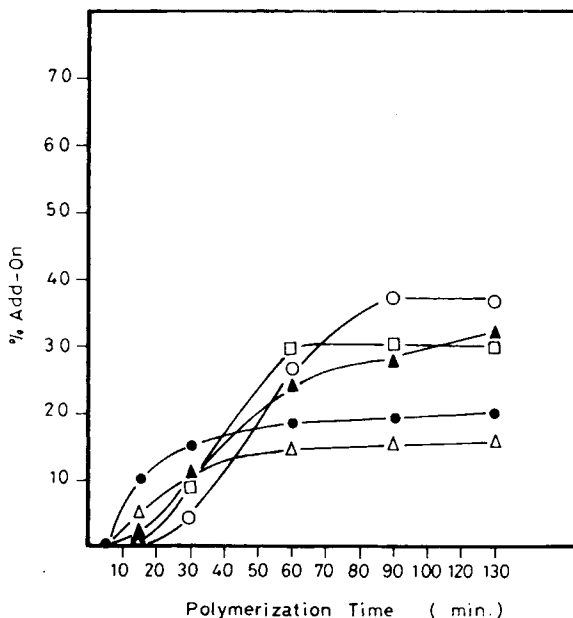


Fig. 8. Effect of reaction time on % polymer add-on.  $[H_2O_2]$ , 0.025%; [thioureadioxide], 0.033%;  $[Fe^{2+}]$ , 0.031%; [monomer or monomer mixtures], 50% based on weight of fabric; 4 drops Emalpur P; reaction temperature = 60°C; material-to-liquor ratio, 1:30. (○) GMA; (●) GMA/Aam (8:2); (△) GMA/AN (8:2); (▲) GMA/Styrene (8:2); (□) GMA/BMA (8:2).

where the add-ons obtained with GMA are higher than those obtained with its mixtures.

### Contribution Of GMA in the Add-on

Cotton samples containing different poly(GMA–Aam) add-ons were analyzed for the epoxy content as well as for nitrogen content. The polymer add-ons which originally derived from the increase in weight of the fabric were recalculated on

TABLE I  
Cotton Samples Containing Different Poly(GMA–Aam) Add-ons as Determined via Weight Difference, Estimation of Epoxy Content and Nitrogen Content

Type of monomers used	Total polymer add-on (w/w, %)	% GMA rest found	% nitrogenic rest found
GMA:Aam 8:2	10.7	8.12	0.65
	34.8	19.96	1.70
	37.4	23.60	2.00
	49.9	20.84	3.00
GMA:Aam 5:5	5.67	4.05	1.95
	18.70	12.24	5.63
	27.90	15.91	7.33
	38.57	19.93	10.35
GMA:Aam 2:8	5.20	4.03	1.10
	13.20	5.88	4.98
	14.90	4.15	4.79
	19.90	6.84	4.34

TABLE II  
Cotton Samples Containing Different Poly(GMA-AN) Add-ons Determined via Weight Difference, Estimation of Epoxy Content and Nitrogen Content

Type of monomer used	Total polymer add-on (w/w, %)	% GMA rest found	% nitrogenic rest found
GMA:AN	4.1	3.48	0.57
8:2	16.80	15.59	1.39
	27.90	23.71	2.94
	49.90	44.63	3.99
GMA:AN	5.1	4.87	0.80
5:5	12.20	11.88	1.37
	13.86	12.38	2.65
	16.52	14.15	1.49
GMA:AN	2.00	1.50	0.43
2:8	4.70	3.54	1.59
	15.80	12.07	3.28
	14.10	9.52	4.45

the basis of free epoxy ring and nitrogen analyses. The results obtained are given in Table I. The same analyses and recalculation were done with respect to cotton samples containing different poly(GMA-AN). The results obtained are set out in Table II.

It is seen (Table I) that the percent add-ons derived from increase in weight in case of poly(GMA-Aam)-containing cotton are much higher than their mates

TABLE III  
Cotton Samples Containing Different Poly(GMA-BMA) Add-ons as Determined by Difference in Weight and Estimation of Epoxy Content

Type of monomers used	Total polymer add-on (w/w, %)	% GMA rest found	% hydrocarbon rest by difference
GMA:BMA	15.3	11.95	3.35
8:2	43.5	35.50	8.00
	53.2	42.56	10.74
	75.5	60.57	14.93
GMA:BMA	11.7	3.94	7.76
2:8	29.3	9.80	19.50
	39.4	13.16	26.24
	50.4	16.85	33.85

TABLE IV  
Cotton Samples Containing Different Poly(GMA-Styrene) Add-ons as Determined by Difference in Weight and Estimation of Epoxy Content

Type of monomers used	Total polymer add-on (w/w, %)	% GMA rest found	% hydrocarbon rest by difference
GMA:styrene	13.4	12.10	1.30
8:2	39.1	35.08	3.30
	51.4	46.90	4.54
	61.0	56.40	5.60
GMA:styrene	12.3	3.10	9.20
2:8	25.4	6.36	19.08
	36.3	9.09	27.21
	37.1	9.27	27.83

based on epoxy ring and nitrogen analyses. This is observed irrespective of the ratio and concentration of GMA/Aam mixtures used. However, the magnitude of contribution of GMA in the add-on seems to depend essentially upon the ratio of GMA/Aam in the mixture. Current work reveals that the add-on is composed mainly of poly(GMA) when GMA/Aam at a ratio of 8:2 is used. Reversing this ratio, i.e., at a ratio of GMA/Aam of 2:8, brings about add-ons of poly(GMA-Aam) in which the concentrations of GMA and Aam are roughly equal. On the other hand, the contribution of Aam in poly(GMA-Aam) add-on amounts to half of that of GMA when the GMA/Aam mixture at a ratio of 5:5 was used.

Previous work<sup>31</sup> has disclosed that the percent polymer add-ons derived from increase in weight are very comparable with those based on epoxy ring analysis in the case of polymerization of GMA with cotton cellulose. An indication of this is that the free epoxy rings were not involved in any reaction during polymerization. With this in mind, the lower add-ons based on epoxy and nitrogen contents as compared with their mates derived from the increase in weight (Table I) suggest that addition of amide groups of Aam to the epoxide groups of GMA occurs.

Table II shows that the percent polymer add-ons derived from increase in weight are comparable with those based on epoxy ring and nitrogen analyses in case of poly(GMA-AN), opposite to poly(GMA-Aam). This indicates that the free epoxy rings did not undergo any reaction during polymerization of a mixture of GMA/AN with cotton cellulose regardless of the ratio or concentration of the mixture used. However, contribution of GMA in the poly(GMA-AN) add-on depends upon its ratio in the mixture. Contribution of GMA in the add-on is pronounced at GMA/AN ratios of 8:2 and 5:5 and decreases at a ratio of 2:8.

Tables III and IV show the contribution of GMA in the add-on in case of poly(GMA-BMA)- and poly(GMA-styrene)-containing cotton, respectively. Assuming that no epoxide ring is involved in any reaction, the results indicate that the contribution of GMA in the add-on amounts to about 80% and 33% when the GMA/BMA mixtures at ratios of 8:2 and 2:8 are used, respectively. This contrasts with GMA contribution of about 90% and 25% when the GMA/styrene mixtures were used under similar conditions. An indication of this is that the magnitude of contribution of GMA in the add-on is governed by the nature of the monomer used along with it as well as the ratio of GMA in the mixture.

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