

# Graft Copolymerization of Methyl Methacrylate and Other Vinyl Monomers onto Cotton Fabric Using Ferrous Cellulose Thiocarbonate–*N*-Bromosuccinimide Redox Initiation System

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## SYNOPSIS

The cellulose thiocarbonate, in the fabric form, was treated first with a freshly prepared ferrous ammonium sulphate (FAS) solution. The so-treated fabric formed, with *N*-bromosuccinimide (NBS), an effective redox system capable of initiating grafting of methyl methacrylate (MMA) and other vinyl monomers onto the cotton fabric. The effect of the polymerization conditions on the polymer criteria, namely, graft yield, homopolymer, total conversion, and grafting efficiency, was studied. These polymer criteria were found to depend extensively upon concentrations of the  $\text{Fe}^{2+}$  ion (activator), NBS (initiator), and MMA; pH of the polymerization medium, and duration and temperature of polymerization. Based on detailed investigation of these factors, the optimal conditions for grafting were as follows:  $\text{Fe}^{2+}$ ,  $1 \times 10^{-3}$  mol/L; NBS,  $1 \times 10^{-2}$  mol/L; MMA, 4%; pH, 2; polymerization time, 150 min; polymerization temperature, 60°C; material/liquor ratio, 1 : 100. Under these optimal conditions, the rates of grafting of different vinyl monomers were in the following sequence: methyl methacrylate  $\gg$  methyl acrylate  $>$  acrylonitrile. Other vinyl monomers, namely, acrylic acid, and methacrylic acid have no ability to be grafted to the cellulosic fabric using the said redox system. A tentative mechanism for the polymerization reaction is suggested.

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## INTRODUCTION

Many reports have dealt with employment of *N*-bromosuccinimide (NBS) as a brominating agent for a number of unsaturated aliphatic and aromatic hydrocarbons, some ester and carbonyl compounds, etc.<sup>1–9</sup> However, the use of NBS as an initiator for aqueous vinyl polymerization is comparatively limited,<sup>10–13</sup> and its use for grafting of vinyl monomers onto textile fibres is very limited.<sup>14</sup> The NBS was directed only as a photoinitiator for vinyl grafting reaction. To the knowledge of the author, no work has reported on the graft copolymerization reactions onto textile fibers us-

ing NBS in conjunction with a reduced metal salt as a redox initiation system.

The present work reports graft copolymerization of methyl methacrylate (MMA) onto cotton fabric using ferrous cellulose thiocarbonate–NBS redox system. The ability of this initiation system to induce grafting of other vinyl monomers (acrylic acid, methacrylic acid, methyl acrylate, and acrylonitrile) onto the same substrate was also examined.

## EXPERIMENTAL

### Preparation and Purification of Materials

#### NBS

The NBS (Araphoe Chemicals, Inc.) was prepared by rapid recrystallization from ten times

its weight of boiling water, followed by drying in air as described in detail elsewhere.<sup>15</sup> To minimize the formation of molecular bromine, the recrystallized NBS (white) was stored in a brown stoppered glass bottle and kept at 5°C. A stock aqueous solution of the purified NBS was prepared just prior to use.

### **Vinyl Monomer**

Stabilized MMA, methyl acrylate (MA), acrylonitrile (AN), methacrylic acid (MAA), and acrylic acid (AA) were carefully distilled before use.

### **Ferrous Ammonium Sulphate (FAS)**

To minimize the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> ions by air oxygen, an aqueous solution was prepared just prior each experiment, using analytical reagent-grade ferrous ammonium sulphate (Mohr's salt), [FeSO<sub>4</sub> · (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6H<sub>2</sub>O], of at least 99.5% purity.

### **Other Chemicals**

Carbon disulphide (CS<sub>2</sub>), sodium hydroxide, ammonium hydroxide, and sulphuric acid were reagent-grade chemicals.

### **Thiocarbonation of Cotton Fabric**

The procedure of cotton fabric thiocarbonation has been described in an earlier publication.<sup>16</sup>

### **Treatment with FAS**

The thiocarbonated cotton fabric was treated with 100 mL of aqueous solution of FAS of specified concentration at 30°C for 30 min under continuous shaking. This was followed by washing the sample thoroughly with distilled water to remove the unadsorbed Fe<sup>2+</sup> ions from the sample surface, then squeezing between two filter papers before introducing to the grafting solution. The fabric in this form will be referred to as ferrous cellulose thiocarbonate (reducing agent).

### **Graft Polymerization Procedure**

Unless otherwise stated, the graft polymerization reaction was carried out as follows. Conditioned cellulose sample was steeped in a 100 mL stoppered glass vessel containing the grafting solution at a specified temperature using a material to liquor ratio of 1 : 100. The grafting solution consisted of known concentrations of NBS and the mono-

mer. The pH of the reaction medium was adjusted before starting the grafting reaction. During the reaction, the cellulosic material was kept well immersed in the solution. The contents of the reaction vessel, throughout the reaction period, were shaken robustly from time to time to shun precipitation and the heaping up of the homopolymer all over the sample surface. After the specified time interval, the reaction was arrested by simultaneous quenching the vessel in the ice cold water and adding hydroquinone to the reaction mixture. The homopolymer, along with the grafted fabric sample, were filtered off, washed repeatedly with water, and dried in an oven at 105°C to constant weight. Finally, the sample was extracted with water or a proper solvent, depending upon the nature of the homopolymer to be removed. Extraction was reiterated until constant weight. The grafted cellulose sample and the free homopolymer were then dried and weighed.

The percentages of graft yield (%GY), homopolymer (%HP), total conversion (%TC), and grafting efficiency (%GE) were calculated as follows.

$$\%GY = \frac{W_2 - W_1}{W_1} \times 100 \quad \%HP = \frac{W_3}{W_4} \times 100$$

$$\%TC = \frac{W_5 + W_3}{W_4} \times 100 \quad \%GE = \frac{W_5}{W_5 + W_3} \times 100$$

where  $W_1$  = dry weight of original sample,  $W_2$  = dry weight of grafted sample,  $W_3$  = weight of homopolymer,  $W_4$  = weight of monomer used, and  $W_5$  = weight of grafted polymer.

## **RESULTS AND DISCUSSION**

### **Tentative Mechanism of Grafting Reaction**

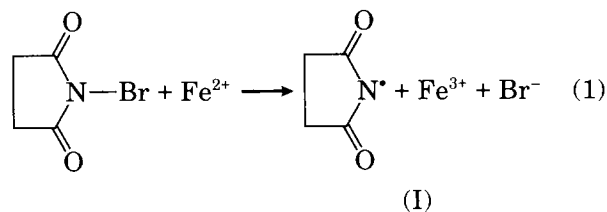
Preliminary experiments made in this work indicated (a) that NBS (oxidant) can easily initiate vinyl grafting reaction onto cotton fabric using ferrous cellulose thiocarbonate (reductant); (b) that the formation of homopolymer could be minimized when the cellulose thiocarbonate sample was pretreated with FAS solution, adversely when the latter was admixed with the grafting solution and followed by immersing the thiocarbonate sample in a such solution; (c) that NBS alone can not initiate the grafting reaction in absence of either Fe<sup>2+</sup> ions or thiocarbonate groups or both; and (d) that the grafting reaction onto the cotton fabric using the ferrous cellulose thiocarbonate-

NBS redox initiation system is inhibited by hydroquinone.

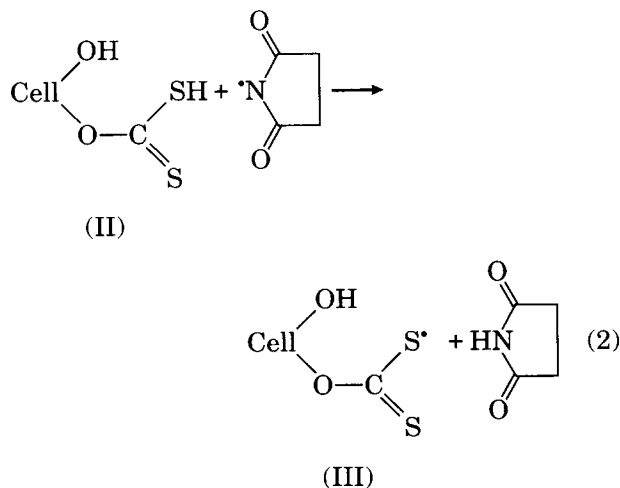
Based on the aforementioned facts, the most probable mechanism of grafting reaction that fits the results may be written as shown in 1-10.

### Initiation

The NBS characterizes by a planar structure, an almost nonpolar N—Br bond. Therefore, it can react easily with  $\text{Fe}^{2+}$  ions by an oxidation-reduction-decomposition reaction to form *N*-succinimidyl radicals (I) and ferric and bromide ions:

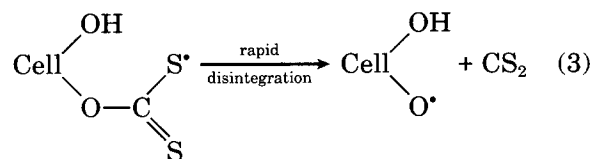


Generation of the *N*-succinimidyl radicals (I) is greatly accelerated in strongly acidic medium. These radicals have no ability to abstract H-atoms from the cellulose hydroxyls; disinclination of the cellulose itself to be grafted with MMA using NBS alone or in coupling with  $\text{Fe}^{2+}$  ions proves this. Nevertheless, the *N*-succinimidyl radicals (I), in addition to their ability to initiate homopolymerization of MMA, are capable of abstracting the more mobile H-atoms from the cellulose thiocarbonate (II) to form primary cellulose thiocarbonate radicals (III) and succinimide molecules:

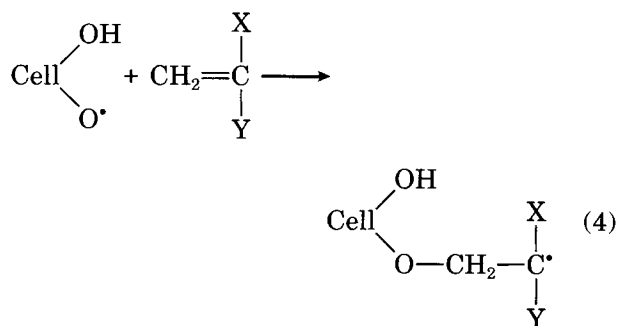


The initially formed thiocarbonate radicals are very unstable; therefore, they will speedy disintegrate to form the most stable cellulose macroradicals (IV) and  $\text{CS}_2$ .<sup>17</sup> The rate of initial radical decom-

position is favored considerably by increase in temperature:

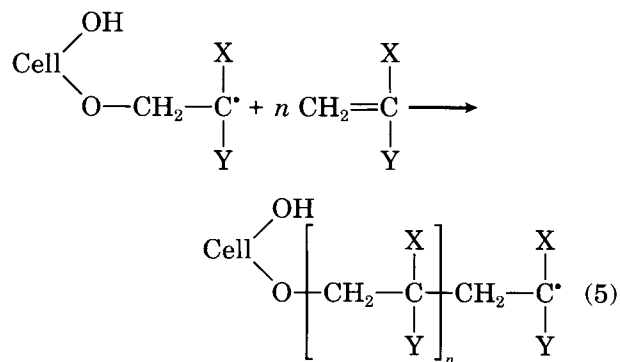


Once the cellulose macroradicals (IV) are formed, they readily attack the vinyl monomer in the immediate vicinity to initiate chain propagation:



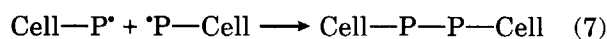
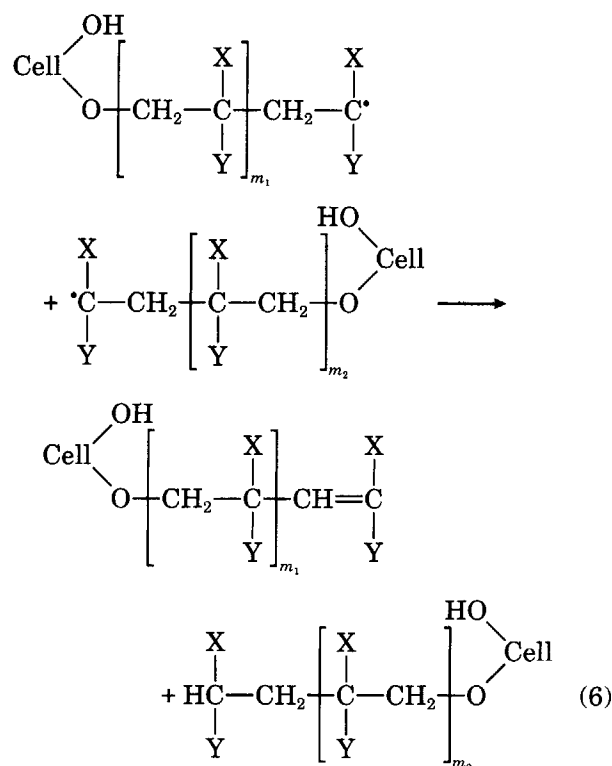
where X is H or  $\text{CH}_3$ ; Y is CN, COOH or COO-alkyl.

### Propagation

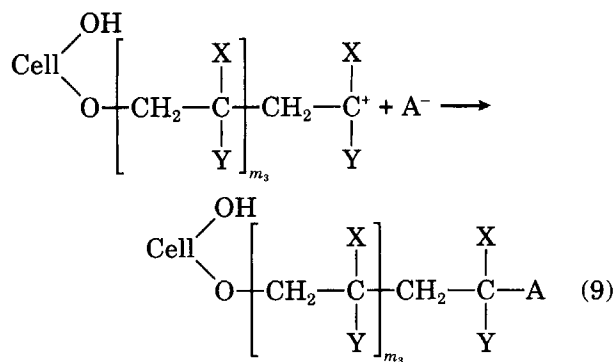
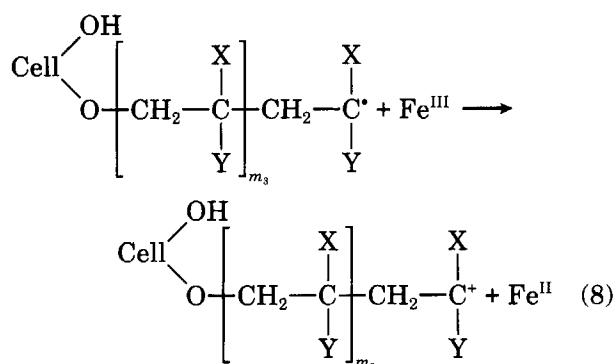


### Termination

The propagating chain of cellulose may be terminated via disproportionation (6) and/or recombination between two growing chains (7):



Termination of the growing grafted chain radical may also occur via the electron transfer mechanism<sup>18</sup> (8 and 9).



where  $\text{A}^-$  represents the anions such as  $\text{Br}^-$ ,  $\text{HSO}_4^-$ ,  $\text{OH}^-$ , etc., which may be produced during the course of the grafting reaction.

With the above tentative mechanism in mind, experiments were designed to study major factors affecting the graft polymerization of MMA. Factors studied include concentrations of NBS and  $\text{Fe}^{2+}$  ion, pH of the polymerization medium, duration and temperature of grafting, and nature and concentration of monomer.

### NBS Concentration

Figure 1 shows the dependence of graft yield ( $GY$ ), homopolymer ( $HP$ ), total conversion ( $TC$ ), and grafting efficiency ( $GE$ ) on the concentration of NBS (initiator) when graft copolymerization of MMA onto cotton fabric was carried out at  $50^\circ\text{C}$  for 120 min using the ferrous cellulose thiocarbonate-NBS redox system. As shown in Figure 1, the  $GY$  increases with increasing the concentration of NBS from  $1 \times 10^{-4}$  up to  $1 \times 10^{-2}$  mol/L. Beyond the latter, the  $GY$  decreases.  $TC$  (to a limited extent) and  $HP$  (to a more limited extent) are both like  $GY$ .  $GE$ , contrary to other polymer criteria, decreases with increasing

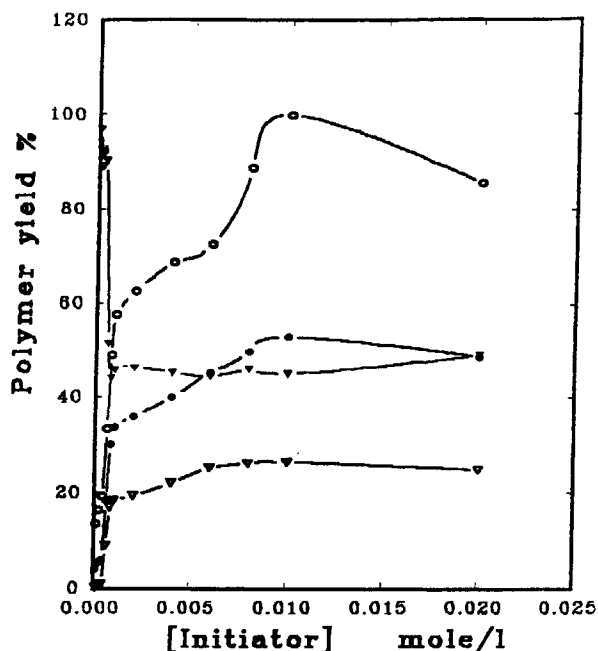
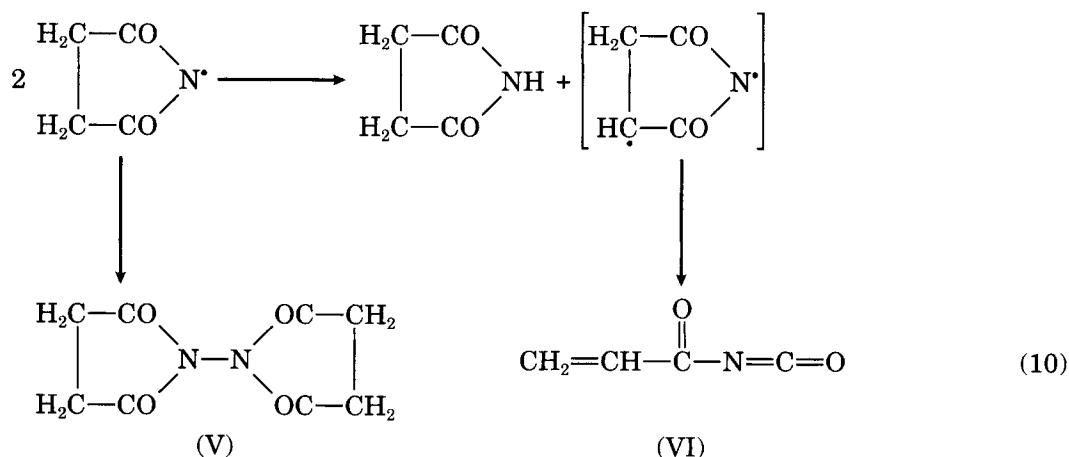


Figure 1 NBS concentration versus percentage of polymer yield and percentage of graft efficiency: (○) % $GY$ ; (▽) % $HP$ ; (●) % $TC$ ; (▼) % $GE$ . Activator,  $1 \times 10^{-3}$  mol/L; MMA, 4%; grafting temperature,  $50^\circ\text{C}$ ; grafting time, 120 min; pH 2; material : liquor ratio, 1 : 100.

NBS concentration in the range of about  $1 \times 10^{-4}$  to  $1 \times 10^{-2}$  mol/L; over this, it tends to increase.

The increments in the *GY*, *HP*, and *TC* as the NBS concentration increases up to  $1 \times 10^{-2}$  mol/L could be associated with the successive generation of the *N*-succinimidyl radicals (Scheme 1) and, in turn, the cellulose macroradicals capable of initiating grafting reaction (Schemes 2-4). Number of these

active species reaches a maximum with  $1 \times 10^{-2}$  mol/L of NBS. Nevertheless, above this concentration, the grafting solution would be depleted greatly by the *N*-succinimidyl radicals. Thereupon, they tend to interact with each other to produce not the coupling products, bis-*N*-succinimidyl (V), but instead, other stable products, possibly succinimide and acryl isocyanate (VI) (10)<sup>15,19</sup>:



In addition to the disproportionation reaction (10), the *N*-succinimidyl radicals may participate in the termination reaction of the growing chains. Consumption of *N*-succinimidyl radicals in such a reaction is, of course, responsible for the decrements in the *GY*, *TC*, and *HP* when the highest NBS concentration ( $2 \times 10^{-2}$  mol/L) was used.

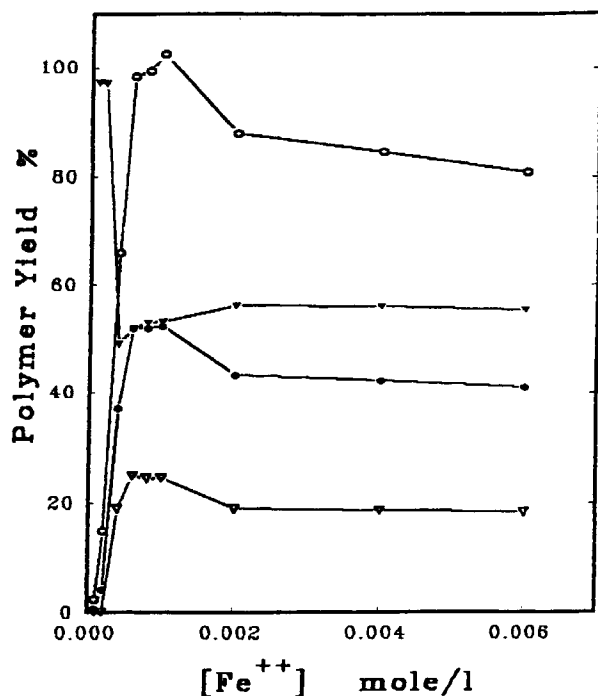
On the other hand, the opposite behavior of *GE* than other polymer criteria is a logical consequence as it is the converse of *HP* behavior, i.e., the grafting efficiency decreases as the homopolymerization increases and vice versa.

### Ferrous Ion Concentration

Figure 2 shows the polymer yields of the thiocarbonated sample as a function of ferrous ion (activator) concentration. The latter represents the ferrous ammonium sulphate (FAS) concentration used in treatment of these samples prior to immersing them in an aqueous grafting solution consisting of NBS ( $1 \times 10^{-2}$  mol/L) and MMA (4%). It is obvious that the *GY* increases sharply as the FAS concentration increases in the lower range of concentration ( $1 \times 10^{-4}$ – $6 \times 10^{-4}$  mol/L). But a maximum was observed at about  $1 \times 10^{-3}$  mol/L; then the *GY* decreases with increasing concentration. The same situation is also encountered with both *TC* and *HP* (Fig. 2).

The behaviour of the polymer criteria within the concentration range  $1 \times 10^{-4}$ – $1 \times 10^{-3}$  mol/L could be interpreted in terms of the oxidation-reduction-decomposition reaction. The latter is greatly accelerated as FAS concentration increases up to  $1 \times 10^{-3}$  mol/L, with the formation of abundant amounts of *N*-succinimidyl radicals and  $\text{Fe}^{3+}$  ions (1). As already mentioned, the *N*-succinimidyl radicals are responsible for generating of cellulose macroradicals as well as monomer radicals. Moreover, the  $\text{Fe}^{3+}$  ion, depending on its concentration in the grafting medium, may act as an initiator as well as a terminator.<sup>18</sup> Stated in other words, the  $\text{Fe}^{3+}$  ion, in a certain range of its lower concentration, is considered to coordinate to the oxygen of the carbonyl group of MMA to form a complex.<sup>20-22</sup> This complex may produce a primary radical capable to initiate the polymerization reactions.<sup>23,24</sup> The synergistic effects of both *N*-succinimidyl radicals and  $\text{Fe}^{3+}$  ions for initiating grafting and homopolymerization reactions of MMA may account for the increments in the yields of *GY*, *HP*, and *TC*.

The fact that the percentages of *HP*, *TC*, and, in particular, *GY* diminish with the FAS concentration higher than  $1 \times 10^{-3}$  mol/L suggests that the *N*-succinimidyl radicals as well as  $\text{Fe}^{3+}$  ions are able to terminate the growing chain radical (6-9) rather than to propagate it. Figure 2 shows also that the



**Figure 2** Percentages of graft yield, homopolymer, total conversion, and grafting efficiency as functions of the ferrous ammonium sulphate concentration: (○) %GY; (▽) %HP; (●) %TC; (▼) %GE. NBS,  $1 \times 10^{-2}$  mol/L; MMA, 4%; temperature,  $50^{\circ}\text{C}$ ; time, 120 min; pH 2; material : liquor ratio, 1 : 100.

GY exhibits the opposite trend than other polymer criteria.

### pH of the Polymerization System

The ability of ferrous cellulose thiocarbonate-NBS redox system to induce graft copolymerization of MMA onto cotton fabric at different pHs is shown in Figure 3. It is clear that the total conversion of MMA to both grafts and homopolymer increases considerably in a strongly acidic medium and attains maximum at pH 2 (i.e.,  $TC \approx 57\%$ ;  $GY \approx 100\%$ ; and  $HP \approx 29$ ). At pH 3, in other words, the polymer criteria, except GE, reach very trivial amounts; and no polymerization reactions occur at pH higher than 3.

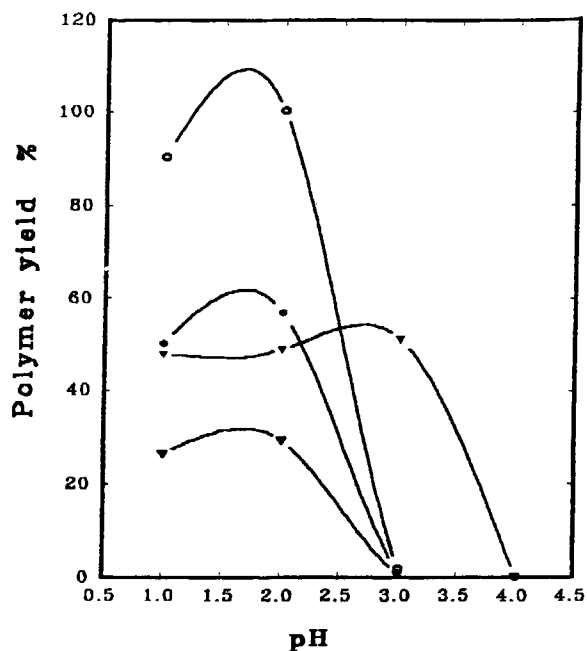
The considerable increments in the polymer criteria at  $\text{pH} \leq 2$  confirm the tremendous enhancement of the oxidation-reduction-decomposition reaction in a strongly acidic medium due to the following:

1. the great height of reduction power of the  $\text{Fe}^{2+}$  ions to be oxidized to the  $\text{Fe}^{3+}$  ions

which, in turn, initiate the polymerization reactions;

2. the rapid decomposition of NBS under the influence of the more efficient  $\text{Fe}^{2+}$  ions to create the *N*-succinimidyl radicals;
3. enhancement of the process of hydrogen atoms abstraction from the cellulose thiocarbonate groups by the *N*-succinimidyl radicals to form the cellulose thiocarbonate radicals; and
4. speedy disintegration of the less stable initially formed cellulose thiocarbonate radicals and formation of the more stable cellulose radicals.

On the other hand, failure of the ferrous cellulose thiocarbonate-NBS redox system to initiate polymerization of MMA onto cellulose at  $\text{pH} \geq 3$  would be expected to result from the conflicting effects [listed above in (1)–(4)] in the grafting medium. Furthermore, at  $\text{pH} \geq 3$ , the  $\text{Fe}^{3+}$  ions outcome during the redox reaction (1) forms a reddish-brown ferric hydroxide (water-insoluble) on fabric surface. The complete precipitation of  $\text{Fe}(\text{OH})_3$ , which occurs at  $\text{pH} = 3.5$ , will result in impeding the diffusion of the active species as well as the monomer molecules from the aqueous phase to the cellulose backbone.<sup>18</sup>



**Figure 3** Effect of the polymerization medium on the rate of the grafting reaction: (○) %GY; (▽) %HP; (●) %TC; (▼) %GE. NBS,  $1 \times 10^{-2}$  mol/L;  $\text{Fe}^{2+}$ ,  $1 \times 10^{-3}$  mol/L; MMA, 4%; temperature,  $50^{\circ}\text{C}$ ; time, 120 min; material : liquor ratio, 1 : 100.

### Polymerization Temperature

The effect of polymerization temperature on the rates of polymerization, expressed as graft yield, total conversion, and grafting efficiency is shown in Figure 4. A perusal of the results indicates the following: (1) The rate of grafting accelerates by raising the polymerization temperature from 30 to 60°C and reaches maximum at the latter. This is valid during the first 120 min. However, at the later stages of polymerization, the rate of grafting at 50°C is somewhat greater than at 60°C, and then follows the following order: 50 > 60 > 40 > 30°C. (2) The rates of *HP* and *TC* favor by raising the polymerization temperature, particularly during the initial stages of polymerization. Nevertheless, minimum or even no amounts of homopolymer are formed at 25°C during the whole course of reaction. (3) The rate of *GE* decreases with increasing the polymerization temperature, as is anticipated.

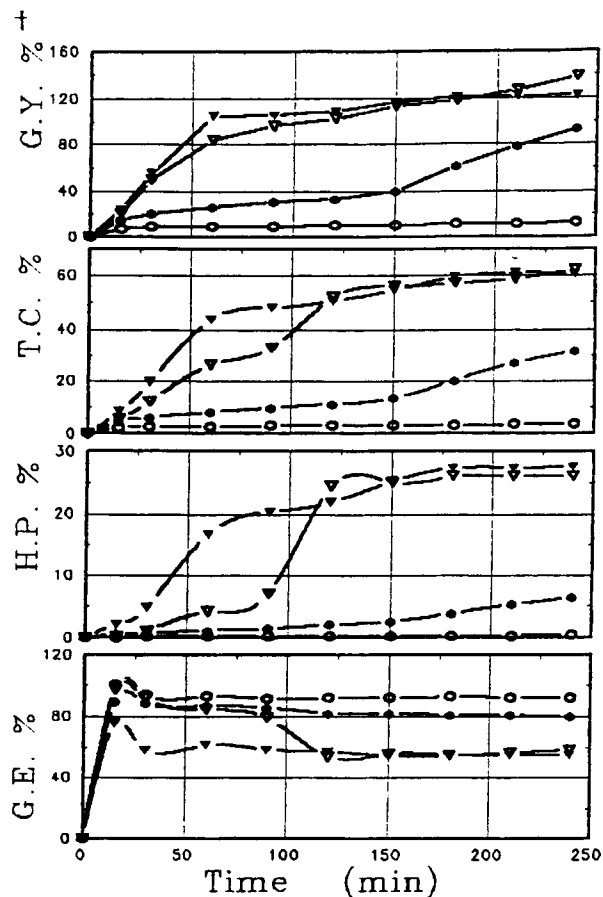
The acceleration of the polymerization rates upon raising the temperature suggests that the latter performs the following functions<sup>25</sup>: (1) Intensifying decomposition of the redox system in question, giving rise to more free radical species; (2) speeding up the disintegration of the thiocarbonate groups; (3) accentuating the swelling properties of cotton fibers; (4) ameliorating the solubility of MMA and its diffusion from the solution phase to the fiber phase; and (5) enhancing the rates of initiation and propagation of the polymer chains.

On the other hand, the slight decrement in the grafting rate at 60°C as compared to that at 50°C during the later stages of polymerization might be due to prevailing the homopolymerization and/or termination reactions over the propagation reaction.

Contrary to its amounts at 60°C, the *HP* attains not striking amounts at 25°C (room temperature); this would provide a rational explanation for reaching the *GE* % of the maximum values at 25°C.

### Duration of Polymerization

Figure 4 also shows the effect of the duration of the polymerization on the *GY*, *HP*, *TC*, and *GE*. As is evident, the polymerization reaction, except at 40°C, is characterized by an initial fast rate followed by a slower one; in most cases, the percentage of polymer yield tends to level off. Levelling off of the percentage of polymer yield could be attributed to depletion in both the monomer and initiator, as well as to the changes in the components of the system as the reaction proceeds.



**Figure 4** Dependence of the grafting rate on the polymerization temperature: (○) 25°C; (●) 40°C; (▽) 50°C; (▼) 60°C. NBS,  $1 \times 10^{-2}$  mol/L;  $\text{Fe}^{2+}$ ,  $1 \times 10^{-3}$  mol/L; MMA, 4%; material : liquor ratio, 1 : 100; pH 2.

At 40°C, in other words, the rate of generation of the active species and, in turn, the rate of polymerization reaction of MMA begins slowly and is enhanced at the later stages of the polymerization.

### Monomer Concentration

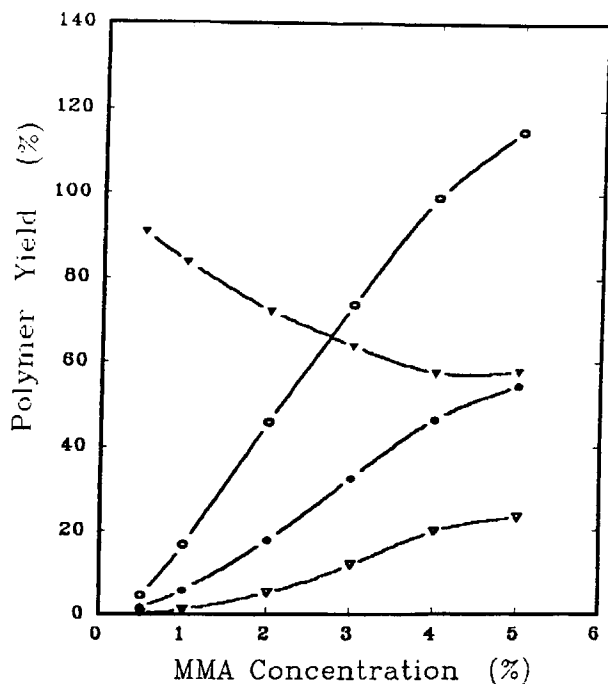
The effect of monomer concentration on extent of the polymer yield was investigated by changing the MMA concentration from 0.5 to 5%. The results are depicted in Figure 5. It can be seen that the higher the grafting, the higher the concentration of MMA in the polymerization system. At a higher concentration of MMA, the gel effect<sup>26</sup> brought about by the solubility of poly(MMA) in its own monomer seems to be more pronounced. As a result, termination of the growing grafted chain radicals is hindered, while the swellability of cotton fabric is enhanced. The ultimate effect of this is increased grafting.

Besides the gel effect, MMA may interact with  $\text{Fe}^{3+}$  ions<sup>20-22</sup> and/or cotton<sup>27,28</sup> to form complexes. Formation of the latter is more favorable at a higher concentration of MMA and cause a further increase in the concentration of the active species in the polymerization medium.

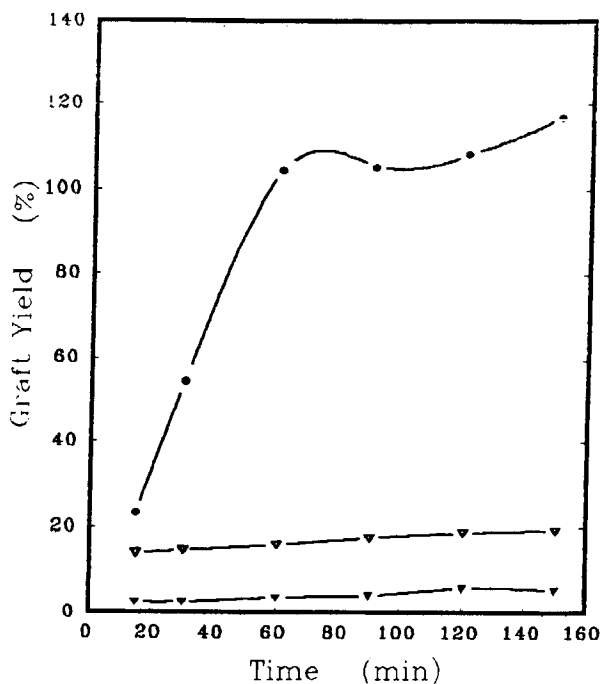
The homopolymerization, the competitive reaction for grafting, is also enhanced at higher MMA concentration because the number of monomer radicals becomes so large. Figure 5 shows also that the graft efficiency and total conversion are largely dependent on the conditions for grafting and homopolymerization.

### Nature of the Monomer

Graft copolymerization was investigated with different vinyl monomers, namely, AA, MAA, MA, and AN, using the ferrous cellulose thiocarbonate-NBS redox system under the optimal grafting conditions obtained with MMA. It is surprising that neither AA nor MAA has an ability to be grafted to the cellulosic fabric. This is probably owing to an interaction is established between the  $\text{Fe}^{2+}$  ions (activator) and the carboxylic groups of both monomer. It is logical to assume that consumption of the  $\text{Fe}^{2+}$



**Figure 5** Influence of methyl methacrylate concentration on the rate of grafting: (○) %GY; (▽) %HP; (●) %TC; (▼) %GE. NBS,  $1 \times 10^{-2}$  mol/L;  $\text{Fe}^{2+}$ ,  $1 \times 10^{-3}$  mol/L; grafting temperature,  $50^\circ\text{C}$ ; grafting time, 120 min; pH, 2; material : liquor ratio, 1 : 100.



**Figure 6** Rates of grafting of cotton fabric using different vinyl monomers: (●) MMA; (▽) MA; (▼) AN. NBS,  $1 \times 10^{-2}$  mol/L;  $\text{Fe}^{2+}$ ,  $1 \times 10^{-3}$  mol/L; monomer, 4%; grafting temperature,  $60^\circ\text{C}$ ; pH, 2; material : liquor ratio, 1 : 100.

ions in a such interaction is responsible for absence of reactive species capable to initiate the polymerization reactions.

Nevertheless, other vinyl monomers (MMA, MA, and AN) can be grafted to the cellulose fabric to different extents. The order of these monomers, as far as percentage of grafting is concerned, follows the following sequence (Fig. 6):



The above order could be explained with respect to polarizability of the vinyl double bond, the ability of the monomer molecules to convert to free radicals, the ability of the monomer radicals to graft and/or homopolymerize, molecular size, and the miscibility and diffusion of the monomer molecules, and/or its radical from the aqueous phase to the fibre phase.

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