

Peroxydiphosphate–Metal Ion–Cellulose Thiocarbonate Redox System-Induced Graft Copolymerization of Vinyl Monomers Onto Cotton Fabric

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ABSTRACT: The grafting of methacrylic acid (MAA) and other vinyl monomers onto cotton cellulose in fabric form was investigated in an aqueous medium with a potassium peroxydiphosphate–metal ion–cellulose thiocarbonate redox initiation system. The graft copolymerization reaction was influenced by peroxydiphosphate (PP) concentration, the pH of the reaction medium, monomer concentration, the duration and temperature of polymerization, the nature of vinyl monomers, and the nature and concentration of metallic ions (activators). On the basis of a detailed investigation of these factors, the optimal conditions for the grafting of MAA onto cotton fabric with the said redox system were as follows: $[\text{Fe}^{2+}] = 0.1 \text{ mmol/L}$, $[\text{PP}] = 2 \text{ mmol/L}$, $[\text{MAA}] = 4\%$, pH-2, grafting time = 2 h, grafting temperature = 70°C, and material/liquor ratio = 1 : 50. Under these

optimal conditions, the graft yields of different monomers were in the following sequence: MAA \gg acrylonitrile $>$ acrylic acid $>$ methyl acrylate $>$ methyl methacrylate. The unmodified cellulosic fabric (the control) had no ability to be grafted with MAA with the PP– Fe^{2+} redox system. The percentage of grafting onto the thiocarbonated cellulosic fabric was more greatly enhanced in the presence of iron salts than in their absence. This held true when the lowest concentrations of these salts were used separately. A suitable mechanism for the grafting processes is suggested, in accordance with the experimental results. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1879–1889, 2003

Key words: initiators; monomers; copolymerization; fibers; graft copolymers

INTRODUCTION

Graft copolymerization onto cellulose has evoked considerable interest from scientists and technologists, as it provides an effective means for synthesizing a series of new products with highly prized properties.^{1–4}

The grafting of vinyl monomers onto cellulose and its derivatives is generally considered to involve the generation of reactive sites on substrate polymers, followed by the addition of a monomer, which propagates in a conventional manner. This can be achieved by several methods; high-energy radiation,^{5–9} low-energy radiation in the presence and absence of sensitizers,^{6,10} and chemical methods.^{11–14} The last method has attracted attention in recent years because it provides direct experimental evidence of the existence of a transient radical intermediate generated by chemical reactions.

Recently, we reported on the grafting of different vinyl monomers onto cotton fabric with cellulose thiocarbonate and different oxidants.^{15–20} Potassium bromate, potassium permanganate acid, hexavalent chro-

mium ion, pentavalent vanadium ion, and ferric ion as oxidizing components were coupled with cellulose thiocarbonate as a reducing component. In a relatively recent study, Zahran²¹ reported on the graft copolymerization of methyl methacrylate (MMA) and other vinyl monomers onto cotton fabric within a ferrous cellulose thiocarbonate-*N*-bromosuccinimide redox initiation system.

Cellulose is chemically modified to the cellulose thiocarbonate substrate before grafting because this modified substrate has a higher reducing power than the original substrate (cellulose), and thus, homopolymer formation can be minimized.

Among the inorganic compounds containing peroxide bonds, peroxydisulfate $[(\text{S}_2\text{O}_8)^{2-}]$ has been used extensively in oxidation studies.^{22,23} The minimum oxidation potential of peroxydiphosphate (PP) is 2.07 V, whereas that of peroxydisulfate is 2.01 V. This indicates that the former should be a slightly stronger oxidizing agent than the latter.

PP ion has been disclosed as a very efficient initiator for aqueous vinyl polymerization.^{24–29} However, its use for grafting vinyl monomers onto natural fibers is very limited.^{30–32} To our knowledge, no studies have yet been published on its utilization for the initiation of vinyl graft polymerization onto chemically modified cellulose. It is the aim of this work to fill this gap.

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EXPERIMENTAL

Cotton fabric

Mill-scoured and bleached cotton fabric (23 picks \times 23 ends/cm), kindly supplied by Misr/Helwan Company (Helwan, Egypt) for spinning and weaving was used as received. Methacrylic acid (MAA), acrylic acid (AA), MMA, methyl acrylate (MA), and acrylonitrile (AN) were used without purification.

Chemicals

Potassium PP was British Drug House (Analar) grade. Iron salts (activators), namely, ferrous ammonium sulfate $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ and ferric ammonium sulfate $[(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ were analytical reagent grade chemicals. All other chemicals were reagent grade.

Procedure

Thiocarbonation of cotton fabric

Thiocarbonation of the cotton fabric was carried out by the introduction of a sample of cotton fabric into a 100-mL stoppered glass vessel containing a freshly prepared solution of sodium hydroxide (1% w/v) and carbon disulfide (1% v/v); the thiocarbonation temperature was kept at 30°C, and the material to liquor ratio was 1 : 50. The contents of the vessel were well shaken from time to time throughout the reaction period. After 1 h, the solution was drained, and the sample was thoroughly washed with distilled water until the washing liquor was pH 7. The sample was then squeezed between two filter papers and dried before it was subjected to further treatment or introduced to the grafting solution. The fabric in this form is referred to as cellulose thiocarbonate.

Metathesis

Metathesis involved the treatment of the thiocarbonated cotton fabric with a solution containing a metal ion reductant (M^{n+}). The cellulose thiocarbonate sample was not likely to react with metal ions that were reducing by themselves, even though chelation could have probably taken place. With regard to this, ferrous ammonium sulfate was used as an efficient M^{n+} .

The thiocarbonated cotton fabric was treated with 50 mL of an aqueous solution of ferrous ammonium sulfate of specified concentration at 30°C for 30 min under continuous shaking. The sample was then washed thoroughly with distilled water to remove the unadsorbed Fe^{2+} ions from the sample surface and then squeezed between two filter papers before it was introduced to the grafting solution. The fabric in this form is referred to as ferrous cellulose thiocarbonate.

Grafting procedure

Unless otherwise stated, the graft polymerization reaction was carried out as follows:

For the metallized-cellulose thiocarbonate fabric. A conditioned cellulose sample was placed in a 100-mL stoppered glass vessel containing the grafting solution at a specified temperature with a material to liquor ratio of 1 : 50. The grafting solution consisted of known concentrations of PP and the monomer. The pH of the reaction medium was adjusted before the grafting reaction was started. The contents of the reaction vessel, throughout the reaction period, were shaken vigorously from time to time to shun precipitation and heaping up of the homopolymer all over the sample surface. After a specified time interval, the reaction was arrested by simultaneous quenching of the vessel in ice water and the addition of hydroquinone to the reaction mixture. The sample was washed thoroughly with water and repeatedly extracted with water or a proper solvent, depending on the nature of the homopolymer to be removed (i.e., whether it was water soluble or water insoluble). Extraction was repeated until a constant weight was reached. The grafted cellulose sample was then dried and weighed.

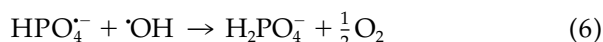
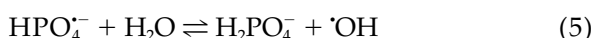
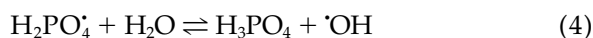
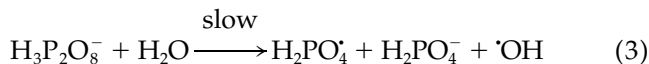
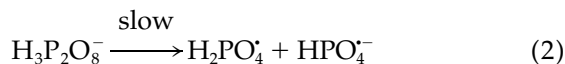
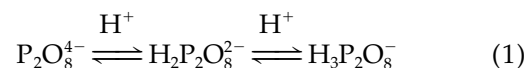
For the cellulose thiocarbonate sample. The thiocarbonated cotton fabric was grafted from a grafting solution consisting of known concentrations of PP, the monomer, and the metal ion oxidant (M^{n+1} ; i.e., ferric ammonium sulfate). The reaction conditions of grafting were then adjusted exactly as mentioned in the previous section.

The percentage graft yield (%GY) was calculated as the percentage of increase in weight over the original weight of the fabric sample.

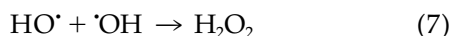
RESULTS AND DISCUSSION

Tentative mechanisms for the initiation of grafting

According to previous reports,³³⁻³⁷ the creation of free-radical species by the decomposition of PP ion in an aqueous and acidic medium is as given by eqs. (1-6):

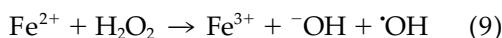
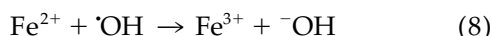


The hydroxyl radicals ($\cdot\text{OH}$) can recombine among themselves to form H_2O_2 :

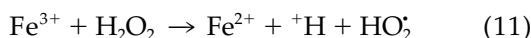
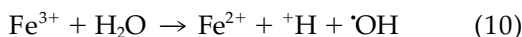


Incorporation of an M^{n+} or M^{n+1} in the initiating system may greatly accelerate the polymerization reactions. This is expected because the presence of a metal ion (either a reductant or an oxidant) may establish an efficient redox system with different active species, intermediates, and/or products formed in the polymerization medium. As a consequence, excessive amounts of free-radical species capable of initiating polymerization reactions (both grafting and homopolymerization) are generated [eqs. (8–11)]:

For an M^{n+} (e.g., Fe^{2+})

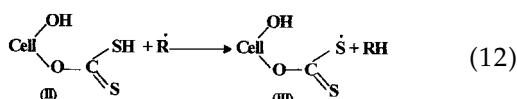


For an M^{n+1} (e.g., Fe^{3+})



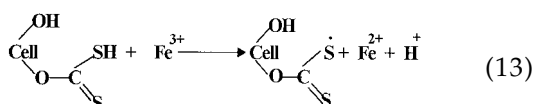
If the active species, such as $[\text{H}_2\text{PO}_4]^\cdot$, $[\text{H}_2\text{PO}_4]^{-\cdot}$, $[\text{HPO}_4]^{-\cdot}$, or $\cdot\text{OH}$, are capable of the abstraction of hydrogen atoms from the thiocarbonate groups ($-\text{C}(\text{SH})\text{S}$) generated along with the cellulose backbone, macroradicals of the latter will be formed. The cellulose macroradicals interact with the monomer, resulting in grafting as represented next.

Initiation

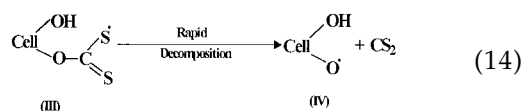


where $\text{R}\cdot$ and RH represent active and inactive species, respectively.

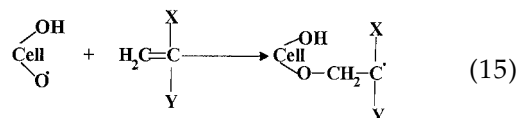
The abstraction of hydrogen atoms from the cellulose thiocarbonate substrate (II) may also occur via the ferric ion when the latter is incorporated in the grafting medium eq. (13):¹⁹



The initially formed thiocarbonate radicals (III) are very unstable; therefore, they will speedily disintegrate to form the most stable cellulose macroradicals (IV) and CS_2 eq. (14):¹⁶

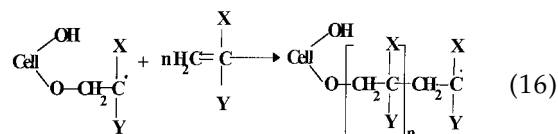


Once the cellulose macroradicals (IV) are formed, they will readily attack the vinyl monomers in the immediate vicinity to initiate chain propagation:



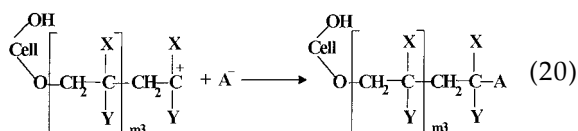
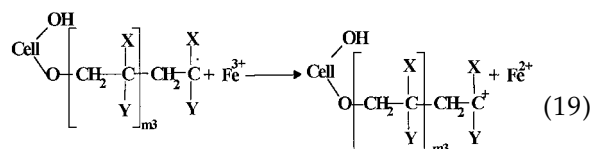
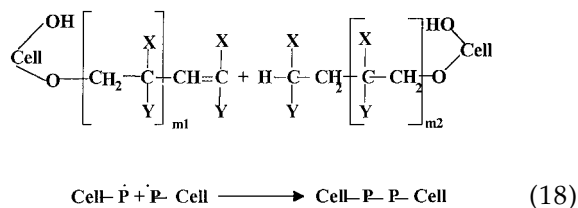
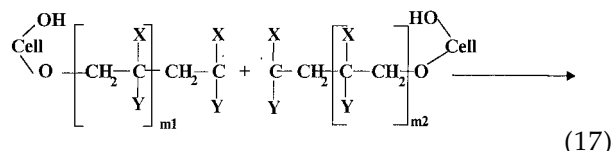
where X is H or CH_3 , Y is $-\text{COOH}$, $-\text{COO}-\text{alkyl}$, or CN .

Propagation



Termination

The termination of grafting may occur by an M^{n+1} , free-radical intermediates, a combination of these, disproportionation, and/or the electron-transfer mechanism eqs. (18–20):¹¹



where A^- represents the anion, such as $[\text{HSO}_4]^-$, $\cdot\text{OH}$, $[\text{HPO}_2\text{O}_8]^{3-}$, $[\text{H}_2\text{P}_2\text{O}_8]^{2-}$, or $[[\text{H}_3\text{P}_2\text{O}_8]^-]$, that may be produced during the course of the grafting reaction.

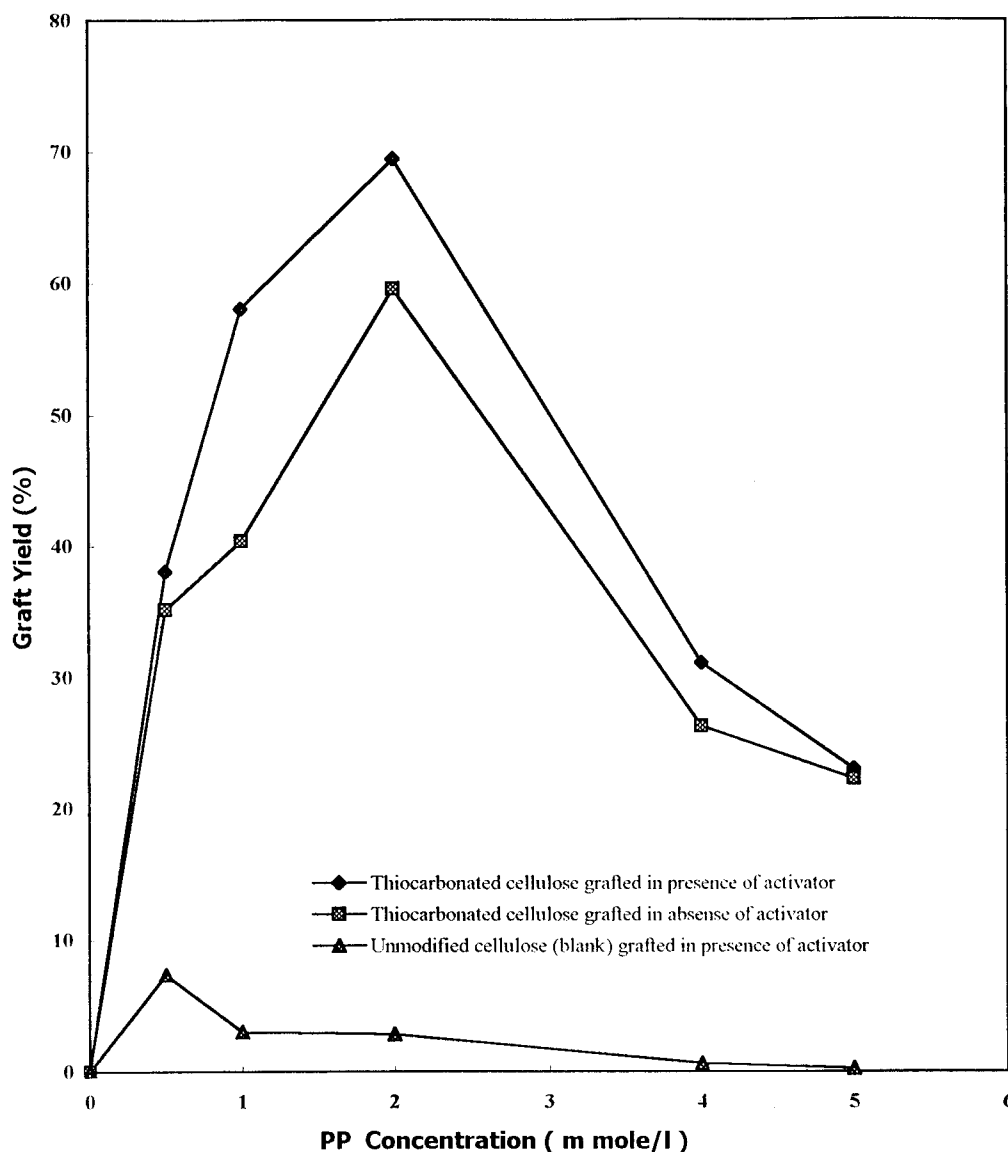


Figure 1 Effect of PP concentration on the graft yield: grafting time = 2 h, grafting temperature = 70°C, [MAA] = 4%, [Fe²⁺] = 0.1 mmol/L, pH = 2, and material : liquor ratio = 1 : 50.

With the previous tentative mechanisms in consideration, we designed experiments to study major factors affecting the graft polymerization of MAA and other vinyl monomers onto cotton fabric with the PP-metal ion-cellulose thiocarbonate redox system. Factors studied included PP concentration, pH of the polymerization medium, the duration and temperature of grafting, the nature and concentration of monomer, and the nature and concentration of the metal ion (activator).

Effect of PP concentration

Figure 1 shows the effect of PP concentration on %GY when MAA was used as vinyl monomer. The concentration of PP was varied from 0.1 to 5 mmol/L, and the concentrations of all other reagents were kept con-

stant. Polymerization was conducted at 70°C for 2 h with a material-to-liquor ratio of 1 : 50. For comparison purposes, the grafting of MAA under the aforementioned conditions was carried out on two substrates, namely, the unmodified cellulose (control) and cellulose thiocarbonate in the absence or presence of 0.1 mmol/L ferrous ammonium sulfate as an activator.

The data of Figure 1 reveal that

1. The PP ion failed to initiate the grafting of MAA onto the unmodified cellulosic substrate (control) in the presence of the Fe²⁺ ion (activator).
2. The incorporation of the hydrosulfide groups (—SH), along with the cellulose backbone, greatly enhanced MAA grafting. Nevertheless, the %GY obtained in the presence of Fe²⁺ ions

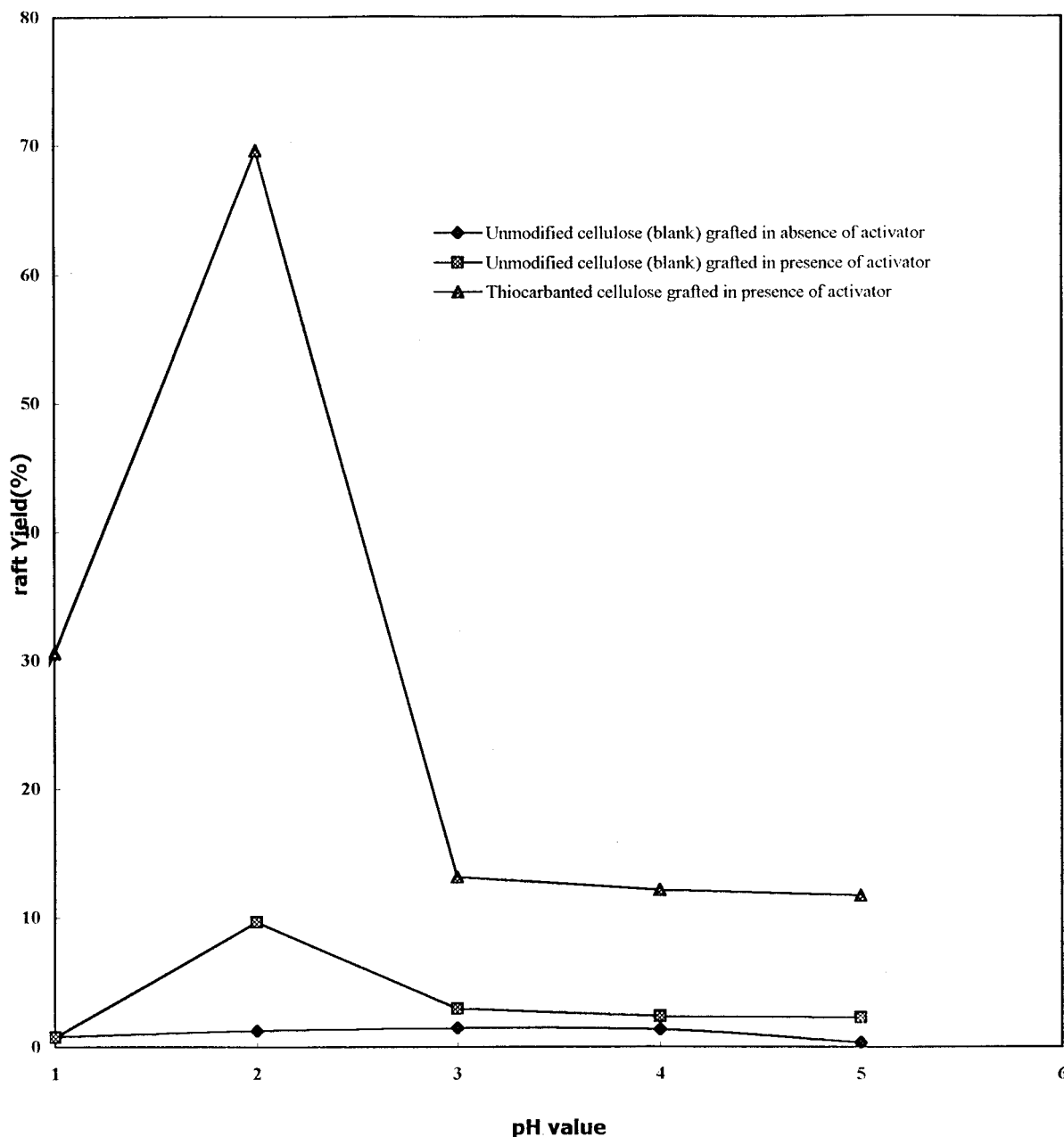


Figure 2 Effect of pH of the polymerization medium on the graft yield: [PP] = 2 mmol/L, [MAA] = 4%, grafting temperature = 70°C, grafting time = 2 h, and material : liquor ratio = 1 : 50.

was higher than in its absence. This confirms that the PP-metal ion-cellulose thiocarbonate system is superior the PP-cellulose thiocarbonate system for the induction of vinyl grafting onto cotton fabric.

- Increasing potassium PP concentration up to 2 mmol/L causes a significant increase in the %GY. Above this concentration, %GY decreased sharply.

The data in Figure 1 may be interpreted in terms of the following:

- Incorporation of the hydrosulfide ($-SH$) groups along the cellulose backbone greatly enhanced the reducing power of the cellulose substrate so as to match the oxidizing power of PP ion. Logically, the weak covalent bonding between the S atom and the H atom greatly facilitated the abstraction of hydrogen atoms from the hydrosulfide groups by various active species (R^{\cdot}) generated in the polymerization medium. This explains the ability of the PP-cellulose thiocarbonate system to induce vinyl graft copolymerization onto cotton fabric. The opposite

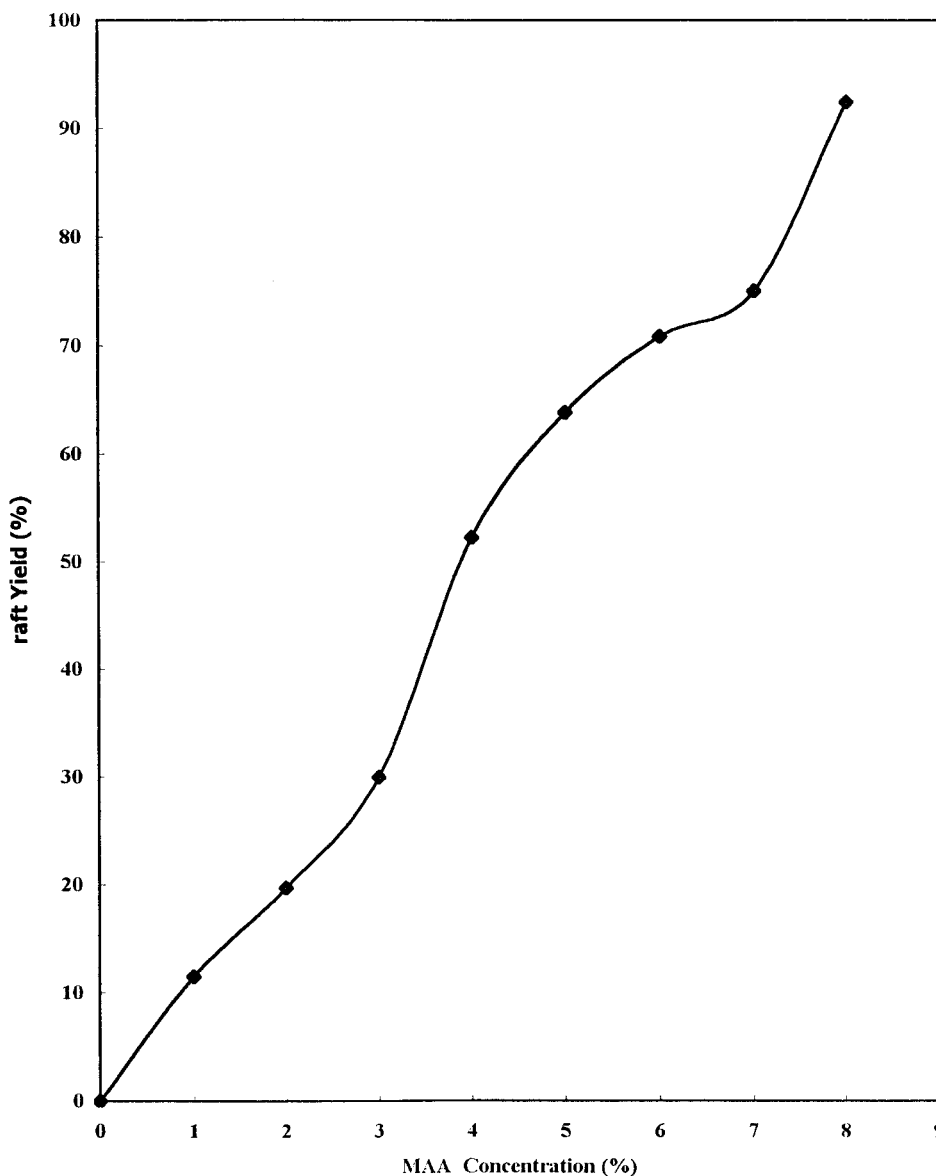


Figure 3 Effect of MAA concentration on the graft yield: [PP] = 2 mmol/L, pH = 2, grafting time = 2 h, grafting temperature = 70°C, [Fe²⁺] = 0.1 mmol/L, and material : liquor ratio = 1 : 50.

holds true for the hydroxyl groups of the unmodified cellulose.

2. Superiority of the PP-Fe²⁺-cellulose thiocarbonate system over the PP-cellulose thiocarbonate system to induce MAA grafting onto cotton fabric was expected because Fe²⁺ would enlarge the reduction level of the cellulose thiocarbonate substrate.³⁸ Moreover, the Fe²⁺ ions generate excessive free radicals and are oxidized to Fe³⁺ ions, which in turn, attack the cellulose thiocarbonate to form the cellulose macroradicals.
3. The increments in %GY caused by increasing the concentration of PP up to 2 mmol/L was due to the formation of a large number of the active species, such as [H₂PO₄][•], [H₂PO₄]^{-•}, [HPO₄]^{-•}, and •OH [eqs. (2–5)]. These radicals abstract hy-

drogen atoms from the (SH) groups, bearing along with the cellulose backbone, giving rise to cellulose radicals at several sites, which facilitates grafting. On the other hand, the decrements in %GY brought about when the concentrations of PP were higher than 2 mmol/L might have been due to the following reasons:³⁹ the large number of free radicals formed could terminate the grafting chain, the oxidant could react with the growing free radicals to give rise to the oxidation product, and at higher concentrations of PP (oxidant), R[•] increased; hence, there was a possibility of the formation of homopolymer, thereby reducing %GY. Moreover, the higher PP concentration led to the production of oxygen.³⁵ The formation of the latter in the polymer-

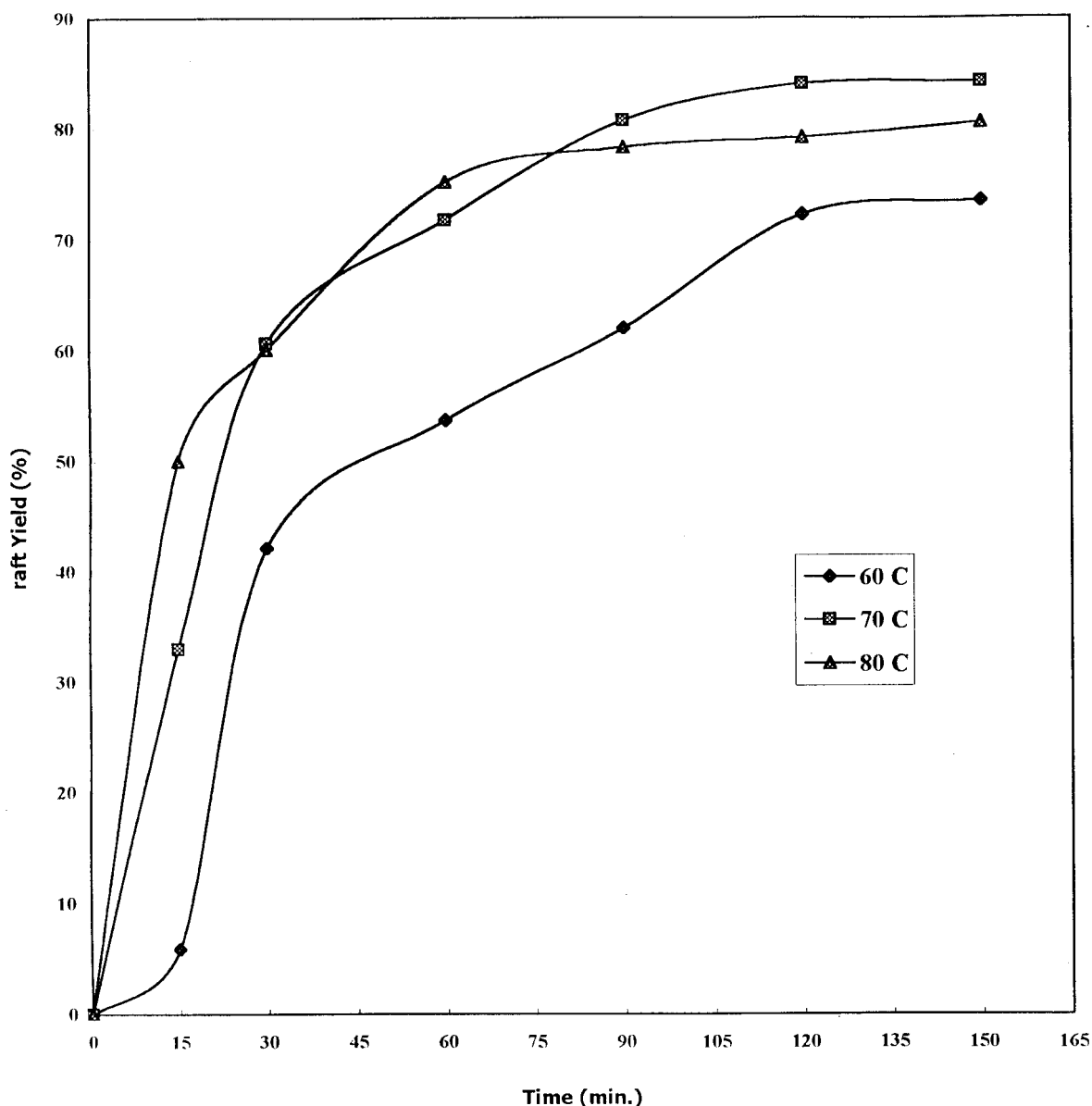


Figure 4 Effect of temperature on the rate of grafting: [PP] = 2 mmol/L, [MAA] = 4%, pH = 2, $[\text{Fe}^{2+}] = 0.1$ mmol/L, and material : liquor ratio = 1 : 50.

ization medium would greatly inhibit the grafting rate.⁴⁰

Effect of pH

To investigate the effect of pH, we carried out the graft polymerization of MAA on to different cotton substrates, namely, unmodified cellulose (blank), thiocarbonated cellulose, and Fe^{2+} -thiocarbonated cellulose, at various pHs, ranging from 1 to 5. Sulfuric acid and ammonium hydroxide were used for pH adjusting. The concentrations of MAA, PP, and ferrous ammonium sulfate were set at 4%, 2 mmol/L, and 0.1 mmol/L, respectively. Polymerization was conducted at 70°C for 2 h at a material to liquor ratio of 1 : 50. The

results of this investigation are shown in Figure 2. It is clear that grafting increased considerably as the pH values increased, attained a maximum at pH-2, and then fell considerably at higher pH values, regardless of the nature of the cellulosic substrates used.

As previously reported,⁴¹⁻⁴³ PP ion ($[\text{P}_2\text{O}_8]^{4-}$) is extensively protonated in acid media due to its high negative charge, which gives rise to various species such as $[\text{HP}_2\text{O}_8]^{3-}$, $[\text{H}_2\text{P}_2\text{O}_8]^{2-}$, $[\text{H}_3\text{P}_2\text{O}_8]^{-}$, $\text{H}_4\text{P}_2\text{O}_8$, $[\text{H}_5\text{P}_2\text{O}_8]^+$, and $[\text{H}_6\text{P}_2\text{O}_8]^{2+}$. It was stated by Maruthamuthy and Santappa^{44,45} that the reaction rate and the concentration of $[\text{H}_3\text{P}_2\text{O}_8]^{-}$ and $[\text{H}_4\text{P}_2\text{O}_8]$ increase with increasing in H^+ concentration. Hence, in a strong medium, that is, at pH of 2 or lower, the most active species, $[\text{H}_3\text{P}_2\text{O}_8]^{-}$, might be formed, which

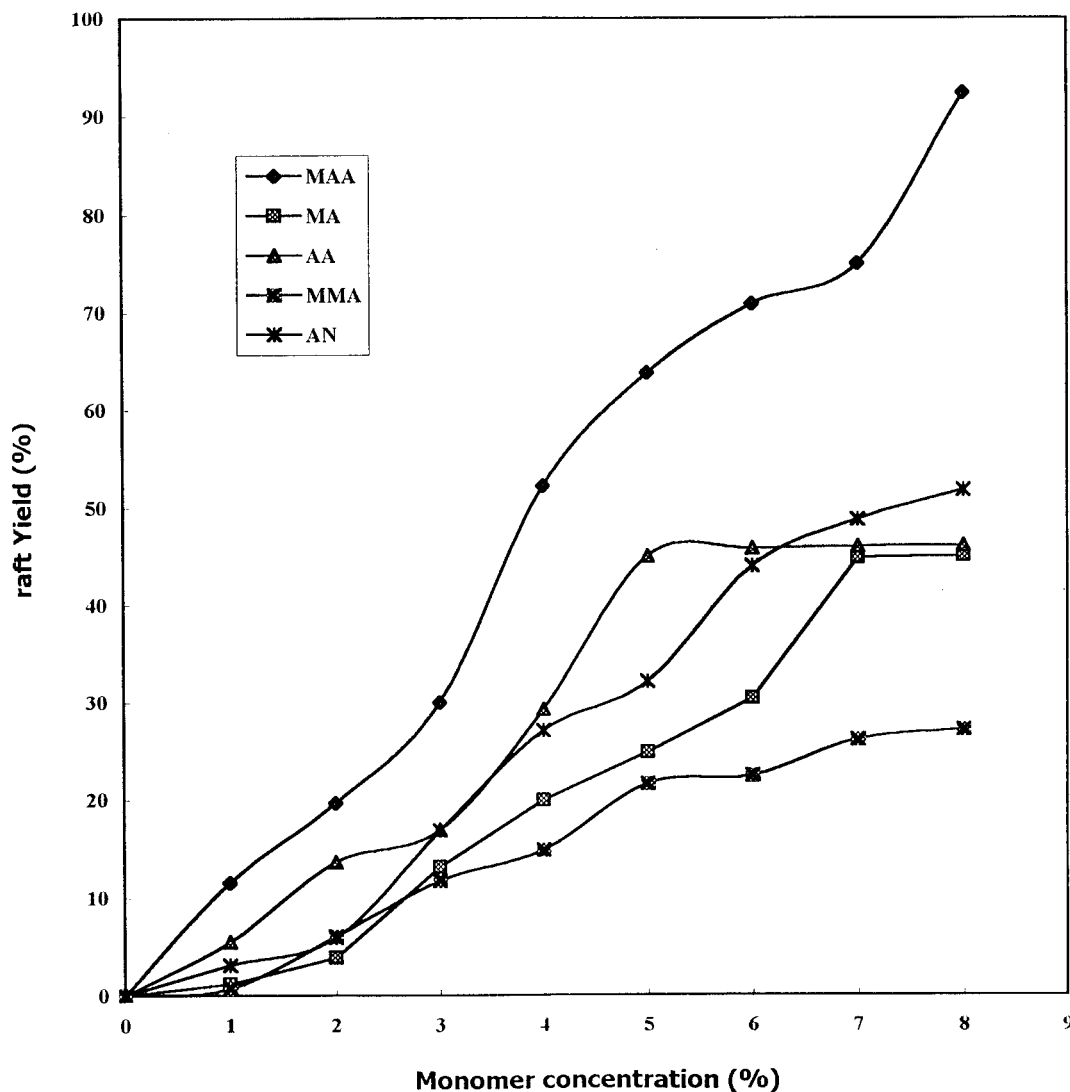


Figure 5 Dependence of the graft yield on the nature of vinyl monomers: [PP] = 2 mmol/L, pH = 2, grafting time = 2 h, grafting temperature = 70°C, $[\text{Fe}^{2+}] = 0.1$ mmol/L, and material : liquor ratio = 1 : 50.

rapidly decomposes and interacts with water, giving rise to a multitude of free radicals [eqs. (2–5)], which enhance grafting. Besides, heightening the acidity of polymerization medium causes²¹ (1) the great height of the reduction power of the Fe^{2+} ions to be oxidized to the Fe^{3+} ions, which in turn, initiate the polymerization reactions, and (2) the speedy disintegration of the less stable initially formed cellulose thiocarbonate radicals and the formation of the more stable cellulose radicals.

On the other hand, the inferiority of the graft yield at pHs of 3 or higher would be expected to result from the conflicting effects (listed in the previous paragraph) in the grafting medium. Furthermore, at pH of 3 or higher, the formation of less active species like $[\text{H}_5\text{P}_2\text{O}_8]^+$ and $[\text{H}_6\text{P}_2\text{O}_8]^{2+}$ might be favored, thereby decreasing %GY.

Effect of MAA concentration

Figure 3 illustrates the effect of MAA concentration on %GY. As is evident, the graft yield is higher, when the concentration of MAA is higher.

The significant enhancement of grafting as the MAA concentration increased (within the range studied) might be due to (1) the favorable effect of the monomer concentration on the production of a large number of growing polymer chains and (2) the increasing swellability of the cellulose fibers, which facilitated diffusion and penetration of various free radicals and the monomer molecules (MAA).

Polymerization temperature

Figure 4 shows the effect of temperature on the rate of grafting of MAA onto cotton cellulose with the PP-

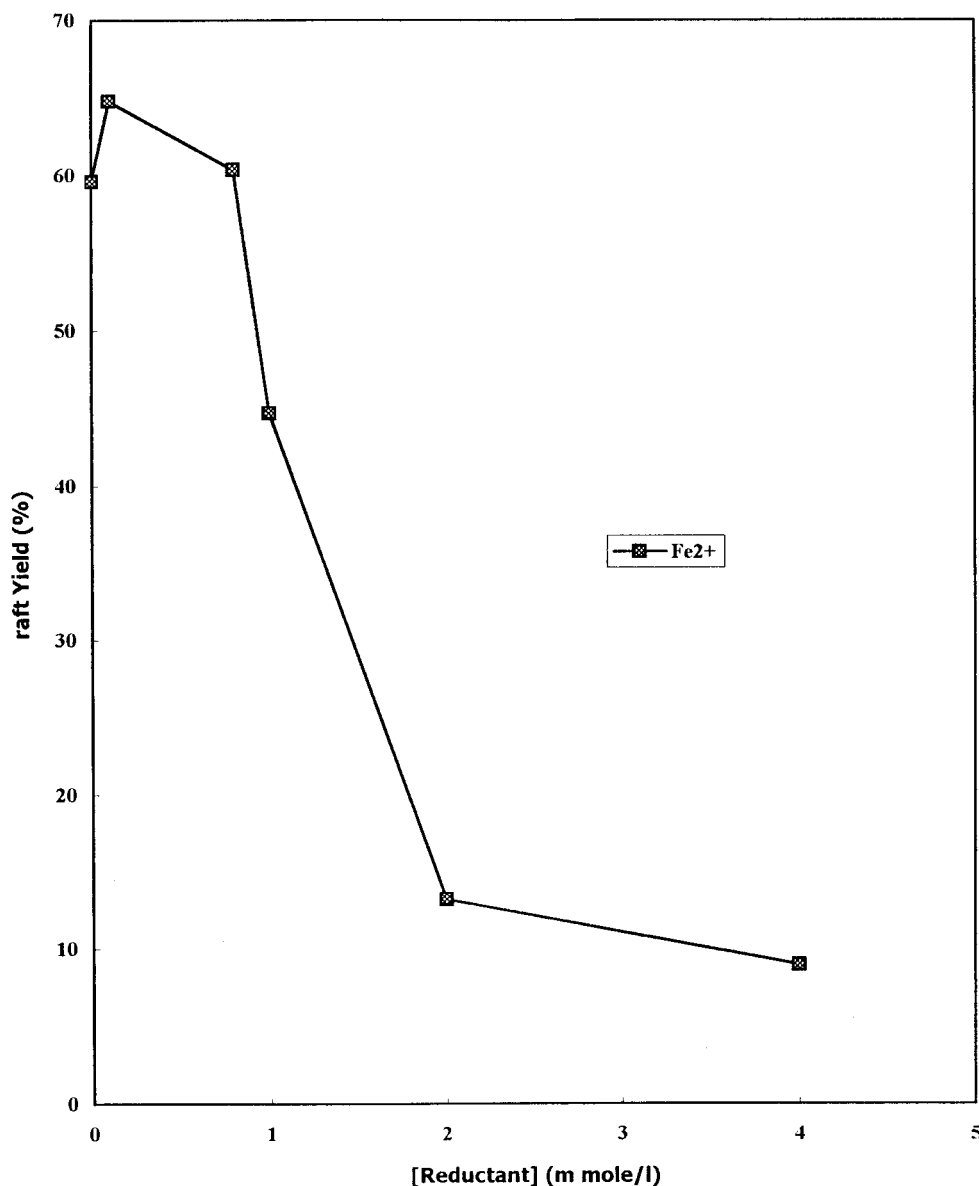


Figure 6 Effect of reductant concentration on the grafting of [MAA]: [PP] = 2 mmol/L, [MAA] = 4%, grafting time = 2 h, pH = 2, grafting temperature = 70°C, and material : liquor ratio = 1 : 50.

Fe²⁺-cellulose thiocarbonate redox system. Obviously, the rate of grafting was temperature-dependent in the order 70 > 80 > 60°C. Thus, 70°C seemed to be the optimum temperature for the grafting of MAA. Although raising the temperature increased the efficiency of the redox system and, in turn, enhanced the rate of the grafting reaction, it also favored the homopolymerization reaction, which would account for the lower magnitude of grafting at 80°C than at 70°C. Nevertheless, the contribution of a faster rate of termination at higher temperature in decreasing the graft yield could not be ruled out.

Figure 4 shows also that irrespective of the temperature, the grafting reaction showed an initial fast rate followed by a slower rate and then leveled off. The leveling off of grafting could be ascribed to the deple-

tion of monomer and initiator concentrations and to the reduction in available active sites on the cellulose backbone as the reaction proceeds.

Nature of the vinyl monomers

The ability of the PP-ferrous cellulose thiocarbonate initiation system to induce the grafting of AA, MA, MMA, and AN onto cotton fabric was studied. The grafting reaction was carried out at the optimal grafting conditions obtained with MAA. The results obtained are shown in Figure 5. For comparison, the results of MAA are also depicted in this figure. It is obvious (Fig. 5) that all of the vinyl monomers in question could be grafted to the cellulose fabric to

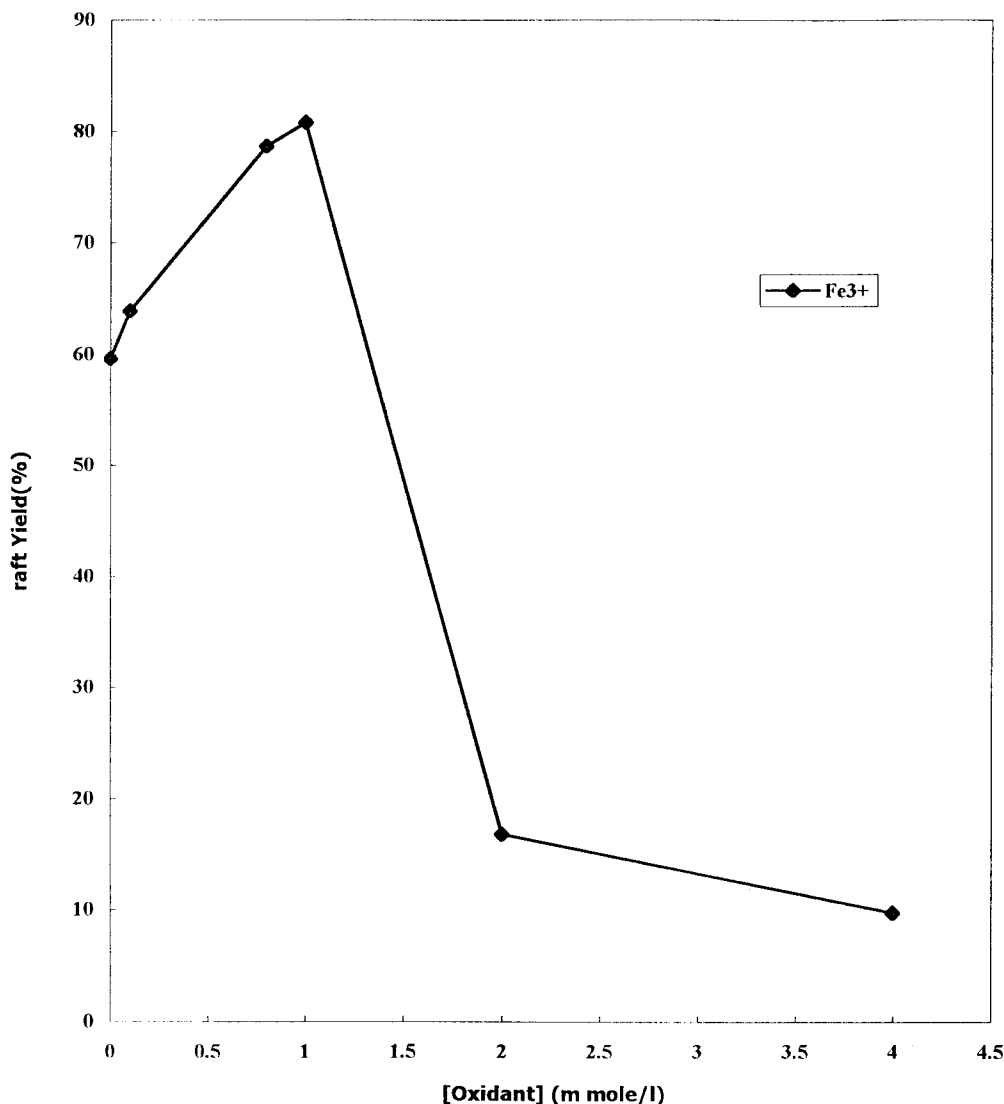


Figure 7 Effect of oxidant concentration on the grafting of MAA: [PP] = 2 mmol/L, grafting time = 2 h, grafting temperature = 70°C, pH = 2, [MAA] = 4%, and material : liquor ratio = 1 : 50.

different extents. The maximum graft yields obtained with these monomers followed the order:



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

Nature and concentration of metal ions (activators)

Metal ion-reductant

Figure 6 shows the dependence of the graft yield on the concentration of ferrous ammonium sulfate (as an M^{n+}). It was adsorbed on the surface of the cellulose

thiocarbonate substrate before it was introduced to the grafting solution. The latter consisted of PP (2 mmol/L) and MAA (4%) at a material to liquor ratio of 1 : 50. The grafting reaction was conducted for 2 h at 70°C. The procedures of metallization of the substrate and the grafting reaction were detailed in the Experimental section. It is clear (Fig. 6) that the lowest Fe^{2+} concentration, which corresponded to 0.1 mmol/L, brought about the maximum graft yield. Beyond this concentration, the graft yield sharply diminished. It was very reasonable to assume that the presence of Fe^{2+} ion at the concentration of 0.1 mmol/L could bring about different free-radical species in the polymerization medium and thence, the graft yield reached maximum. On the other hand, the decrement in grafting with higher Fe^{2+} concentrations suggests that the Fe^{2+} did take part in the termination of the growing polymer chain of the graft and cellulose macroradicals.²¹

Metal ion–oxidant

Figure 7 shows the graft yield as a function of the concentration of ferric ammonium sulfate (as an M^{n+1}) when the latter was mixed with the cotton fabric, MAA, and PP in the polymerization medium. It is evident (Fig. 7) that increasing the ferric ammonium sulfate concentration was accompanied by a successive increment in the graft yield until a concentration of 1 mmol/L ferric ammonium sulfate was reached. Beyond this, the graft yield decreased significantly. The involvement of Fe^{3+} ions in the reactions suggested by eqs. (10, 11, and 13) to yield ultimately free-radical species capable of initiating grafting would account for this.

The decrease in grafting with higher concentrations of ferric ammonium sulfate is in accordance with previous reports.¹⁹ The latter ascribed this to increased termination possibilities with an abundance of free-radical species by recombination in the medium and possible contribution of the Fe^{3+} ion in termination of these species and in termination of the substrate backbone macroradicals .

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