Grafting of Acrylic Monomers onto Cotton Fabric Using an Activated Cellulose Thiocarbonate–Azobisisobutyronitrile Redox System

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ABSTRACT: The feasibility of a cellulose thiocarbonate–azobisisobutyronitrile (AIBN) initiation system to induce graft copolymerization of methyl methacrylate (MMA) and other acrylic monomers onto cotton fabric was investigated. Other acrylic monomers were acrylic acid, acrylonitrile, and methyl acrylate. The initiation system under investigation was highly activated in the presence of a metal-ion reductant or a metal-ion oxidant in the polymerization medium. A number of variables in the grafting reaction were studied, including AIBN concentration, pH of the polymerization medium, nature of substrate, monomer concentration, duration and temperature of polymerization, and composition of the solvent/water polymerization medium. The solvents used were methanol, isopropanol, 1,4-dioxane, cyclohexane, benzene, dimethyl formamide, and dimethyl sulfoxide. There were optimal concentrations of AIBN (5 mmol/L), MMA (8%), Fe^{2+} (0.1 mmol/L), Mn^{2+} (8 mmol/L), and Fe^{3+} (2 mmol/L). A polymerization medium of pH 2 and temperature of 70°C constituted the optimal conditions for grafting. The methanol/water mixture constituted the most favorable reaction medium for grafting MMA onto cotton fabric by using the Fe^{2+}–cellulose thiocarbonate–AIBN redox system. MMA was superior to other monomers for grafting. The unmodified cotton cellulose showed very little tendency to be grafted with MMA compared with the chemically modified cellulosic substrate. A tentative mechanism for the grafting reaction was proposed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1261–1274, 2004

Key words: graft copolymers; initiators; monomers; polymerization; fabrics

INTRODUCTION

2,2′-Azobisisobutyronitrile (AIBN) is one of the most widely used initiators for homopolymerization of vinyl monomers.[1–6] Its use as a free-radical initiator for grafting vinyl monomers onto fibers has also been reported.[7–12] In most grafting reactions, AIBN greatly initiates undesired competitive reactions, among which is homopolymerization. Formation of homopolymer, however, could be minimized by enhancing efficiencies of the substrate and/or initiator to strongly initiate and propagate grafting.

With the above in mind, this work was undertaken with the aim of enhancing efficiencies of the cotton cellulose substrate and the AIBN, to initiate methyl methacrylate and other acrylic monomers (acrylic acid, methyl acrylate, and acrylonitrile) onto the cellulosic fabric sample. To achieve the goal, a mild xanthation (commonly known as thiocarbonation) of cotton cellulose fabric was performed before grafting. Thiocarbonation of the substrate material would provide an effective reducing site on the substrate backbone.[13]

Reducing capacity of the thiocarbonated cotton sample was further enlarged by treating it with known concentrations of metal-ion reductants, particularly the most efficient: ferrous ion.

For comparison purposes, experiments were made by incorporating a metal-ion oxidant in the grafting medium consisting of the cellulose thiocarbonate sample and AIBN. Incorporation of a metal ion-oxidant, particularly ferric ion, would enlarge the efficiency of AIBN for initiating grafting.

Furthermore, the conditions affecting the polymerization reaction were studied. The mechanisms of the free-radical formation are also reported.

EXPERIMENTAL

Preparation and purification of materials

Cotton fabric

Mill-scoured and bleached cotton fabric (23 picks × 23 ends/cm; supplied by Misr/Helwan Company for Spinning and Weaving, Egypt) was used as received without further purification.

Chemicals

Azobisisobutyronitrile (AIBN). AIBN, $(CH_3)_2C(CN)$—N═N—$C(CN)(CH_3)_2$, was recrystallized from toluene.

Monomers. Stabilized acrylic monomers [methyl methacrylate (MMA), methyl acrylate (MA), acrylonitrile (AN), and acrylic acid (AA)] were freshly distilled under reduced pressure and used immediately.

Metallic salts. Analytical reagent–grade ferrous ammonium sulfate [Mohar's salt; $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] and manganous sulfate $(MnSO_4 \cdot H_2O)$ were used separately. To minimize the oxidation of these metal-ion reductants by air oxygen, their aqueous solutions were prepared just before each treatment with the cellulose thiocarbonate sample.

Analytical reagent–grade ferric ammonium sulfate $[(NH_4)Fe(SO_4)_2 \cdot 12H_2O]$ and copper sulfate $(CuSO_4 \cdot 5H_2O)$, as metal-ion oxidants, were used separately in the grafting solution.

Other chemicals

Carbon disulfide (CS_2), sodium hydroxide, sulfuric acid, methanol, isopropanol, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), 1,4-dioxane, benzene, and cyclohexane were reagent-grade chemicals, used as received.

Procedures

Thiocarbonation of cotton fabric

This was carried out by introducing a sample of cotton fabric into a 100-mL stoppered glass vessel containing a freshly prepared solution consisting of sodium hydroxide (1%, w/v) and carbon disulfide (1%, v/v), maintaining the thiocarbonation temperature at 30°C, and using a material/liquor ratio of 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 achieved pH 7. The sample was then squeezed between two filter papers and dried before being subjected to further treatment or being introduced to the grafting solution. The fabric in this form will be referred to as cellulose thiocarbonate.

Metathesis

Metathesis involves treatment of the thiocarbonated cotton fabric with a solution containing a metal-ion reductant. The cellulose thiocarbonate sample is not likely to react with metal ions that are reducing by themselves, even though chelation may probably take place. Concerning this, ferrous ammonium sulfate was used in the initial and greatest part of the work because of its higher reactivity than that of the other reductants examined.

The thiocarbonated cotton fabric was treated with 50 mL of aqueous solution of ferrous ammonium sulfate (or manganous sulfate) 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^{2+} ions from the sample surface, then squeezed between two filter papers before introducing the sample to the grafting solution. The fabric in this form will be 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 using a material/liquor ratio of 1 : 50. The grafting solution consisted of known concentrations of AIBN and the monomer. The pH of the reaction medium was adjusted before starting the grafting reaction. The contents of the reaction vessel, throughout the reaction period, were shaken vigorously from time to time to avoid precipitation and agglomeration of the homopolymer all over the sample surface. After the specified time interval, the reaction was arrested by simultaneously quenching the vessel in ice-cold water and adding 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 the sample achieved constant weight. 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 AIBN, the monomer, and the metallic ion oxidant (i.e., ferric ammonium sulfate or copper sulfate). The reaction conditions of grafting were then adjusted exactly as mentioned for the metallized cellulose thiocarbonate fabric.

The percentage graft yield (%GY) was calculated as follows:

$$\%G.Y. = \frac{W_2 - W_1}{W_1} \times 100$$

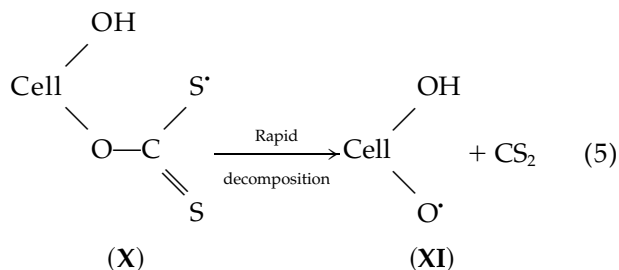where W_1 and W_2 are the weights of the original and grafted samples, respectively.

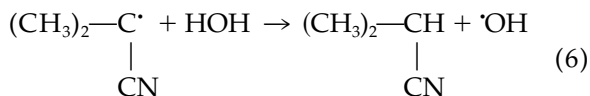### RESULTS AND DISCUSSION

Tentative mechanisms

The thermal decomposition of AIBN was investigated by several workers.[14–17] At temperatures less than 100°C, AIBN decomposes to nitrogen and a resonance-stabilized cyanoisopropyl free radical [eq. (1)]:

$$
:N{\equiv}C{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}N{=}N{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{\equiv}N: \xrightarrow{\text{heat}} \left[\begin{array}{l} \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{\cdot}{C}{-}C{\equiv}N:}} \quad \textbf{(IIa)} \\[2pt] \updownarrow \\[2pt] \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C{=}C{=}N\overset{\cdot}{}:}} \quad \textbf{(IIb)} \end{array} \right] + N_2 \qquad (2)
$$

Resonance–stabilized free radical

The decomposition of AIBN (**I**) is made more complex by the ability of the cyanoisopropyl radical (**IIa**) to react as a radical having structure (**IIb**). The free cyanoisoprpoyl radicals can dimerize to give tetra- methylsuccinodinitrile (**III**) and disproportionate to give isobutyronitrile (**IV**) and methacrylonitrile (**V**). The latter may react with further radicals to give tri- cyano-2,3,5-trimethylhexane (**VI**)[18–20] [eq. (2)]:

$$
\textbf{(IIa)} \rightarrow H_3C{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 + H_3C{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}H H_2C{=}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}} + H_3C{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}H_2C{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \qquad (2)
$$

$$
\quad \textbf{(III)} \qquad\qquad \textbf{(IV)} \qquad \textbf{(V)} \qquad\qquad \textbf{(VI)}
$$

The abnormal recombination of the two resonating forms of the cyanoisopropyl radicals (structures **IIa** and **IIb**) to yield dimethyl-N-(2-cyano-2-propyl)- ketenimine (**VII**) has also been reported[21] [eq. (3)]:

$$
\textbf{(IIb)} \xrightleftharpoons{\text{(IIa)}} \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{=}C{=}N{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CN \xrightarrow{\text{Rearrangement}} \textbf{(III)} \quad (3)
$$

$$
\textbf{(VII)}
$$

The ketenimine (**VII**) is an unstable substance and at higher temperatures (i.e., $\geq 60^\circ C$) it rearranges to tetramethylsuccinodinitrile (**III**).[22] It is also capable of initiating vinyl polymerization[20] (i.e., it is itself a source of radicals). Fission of a C—N bond in the ketenimine to reform two radicals might be expected to occur at a rate almost equal to the rate of fission of C—N bond in the AIBN because the adjacent bonds are similar.[23]

Obviously, of the AIBN decomposition products, only the cyanoisopropyl radicals can initiate polymerization. The cyanoisopropyl radicals (**IIa** and/or **IIb**), in addition to their ability to initiate homopolymerization of MMA, or any other acrylic monomer under investigation, are capable of abstracting the more mobile H-atom from the cellulose thiocarbonate (**IX**) to form primary cellulose thiocarbonate radicals (**X**) and isobutyronitrile (**IV**) [eq. (4)]:

$$
\underset{\underset{O{-}C}{\diagup}}{\overset{\overset{OH}{\diagup}}{Cell}}{\diagdown}\diagup{SH} + \left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{\cdot}{C}{-}C{\equiv}N}} \leftrightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C{-}C{\equiv}N\overset{\cdot}{}}} \right] \rightarrow \underset{\underset{O{-}C}{\diagup}}{\overset{\overset{OH}{\diagup}}{Cell}}{\diagdown}\diagup{S^{\cdot}} + H{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}C{\equiv}N \qquad (4)
$$

$$
\qquad \|S \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \|S
$$

$$
\quad \textbf{(IX)} \qquad\qquad \textbf{(IIa)} \qquad \textbf{(IIb)} \qquad\qquad\qquad \textbf{(X)} \qquad\qquad \textbf{(IV)}
$$

The initially formed thiocarbonate radicals (**X**) are very unstable; therefore, they rapidly disintegrate to form the most stable cellulose macroradicals (**XI**) and CS_2[24] [eq. (5)]. The rate of initial radical decomposition is favored considerably by an increase in temperature:

$$(5)$$

Generation of the hydroxyl radicals ($^\bullet OH$) is also expected to occur according to the following equation:
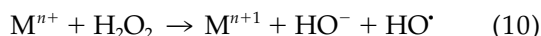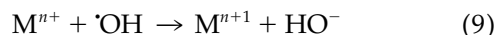
$$(CH_3)_2\!-\!\overset{\displaystyle |}{\underset{\displaystyle CN}{C^\bullet}} + HOH \rightarrow (CH_3)_2\!-\!\overset{\displaystyle |}{\underset{\displaystyle CN}{CH}} + {}^\bullet OH \qquad (6)$$

The $^\bullet OH$ radicals can either recombine among themselves or with some of the other created radicals or can achieve the splitting off of the hydrogen atom from the hydrosulfide group (–SH) bearing along the cellulose backbone [eqs. (7) and (8)]:

$$(7)$$

$$HO^\bullet + {}^\bullet OH \rightarrow H_2O_2 \qquad (8)$$
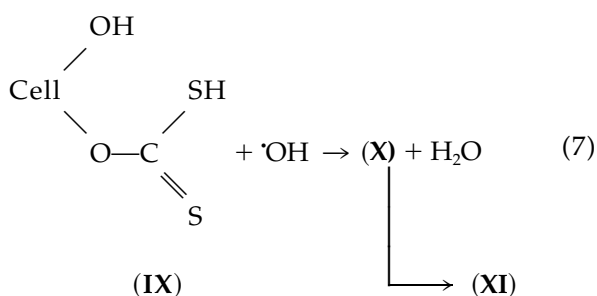
Moreover, because of the presence of oxygen in the polymerization medium, as is the case in all solutions exposed to the air, hydroperoxy radicals, $HOO^\bullet$, are immediately formed from the hydrogen atoms.[25]

Incorporation of a metal-ion reductant (M^{n+}) or a metal-ion oxidant (M^{n+1}) in the initiating system may greatly favor the polymerization reactions.[7] This is anticipated 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 grafting medium. As a consequence, excessive amounts of free radicals capable of initiating polymerization reactions (both grafting and homopolymerization) are generated [eqs. (9)–(15)].

For a metal-ion reductant (M^{n+})

$$M^{n+} + {}^\bullet OH \rightarrow M^{n+1} + HO^- \qquad (9)$$

$$M^{n+} + H_2O_2 \rightarrow M^{n+1} + HO^- + HO^\bullet \qquad (10)$$

For a metal-ion oxidant (M^{n+1})

$$M^{n+1} + H_2O \rightarrow M^{n+} + HO^+ + HO^\bullet \qquad (11)$$

$$M^{n+1} + H_2O_2 \rightarrow M^{n+} + HO^+ + HO_2^\bullet \qquad (12)$$

$$(13)$$

$$M^{n+1} + HC\!-\!(CH_3)_2 \rightarrow M^{n+} + H^+ + {}^\bullet C\!-\!(CH_3)_2$$
$$\qquad\quad \overset{\displaystyle |}{\underset{\displaystyle CN}{}} \qquad\qquad\qquad\quad \overset{\displaystyle |}{\underset{\displaystyle CN}{}} \qquad (14)$$
$$\qquad\quad (\mathbf{IV}) \qquad\qquad\qquad\qquad\quad (\mathbf{II})$$

$$M^{n+1} + H_3C\!-\!\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\!-\!\overset{\displaystyle CH_3}{\underset{\displaystyle CN}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\!-\!CH_3 \rightarrow M^{n+} + (CH_3)_2C\!=\!C\!=\!N^\bullet + (CH_3)_2^\bullet C\!-\!C\!\equiv\!N \qquad (15)$$
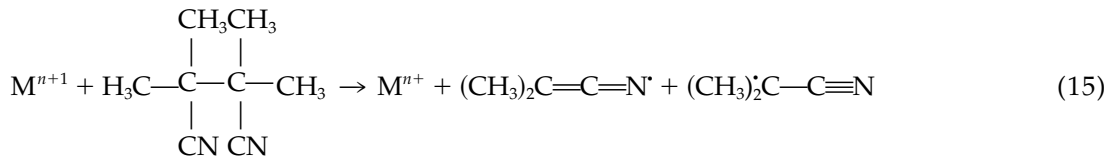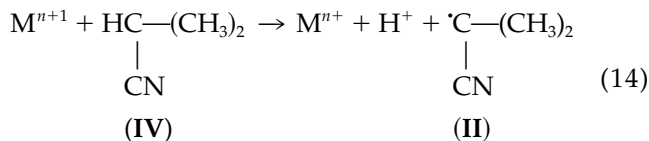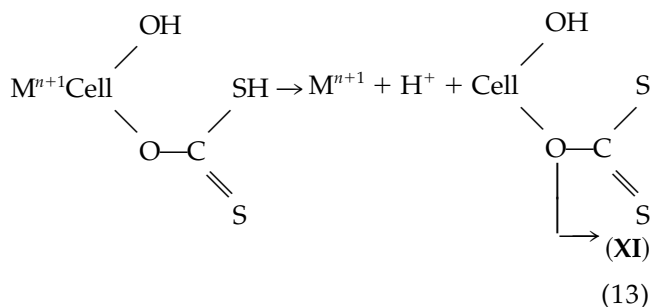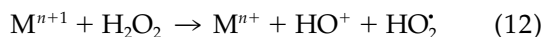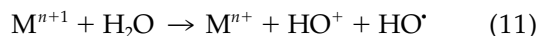
Formation of the cellulose macroradicals (**XI**) [eqs. (5), (7), and (13)] and, in the presence of monomer, grafting would be initiated by the addition of these free radicals to the double bonds of the monomer molecules. The graft yield would be expected to be governed by AIBN concentration, pH of the polymerization medium, temperature and duration of grafting, solvent/water ratio, nature and concentration of monomer, as well as nature and concentration of metal ion (activator). To check the feasibility of this, the aforementioned system was investigated and the results obtained along with their appropriate discussion are presented below.

(a)   (b)
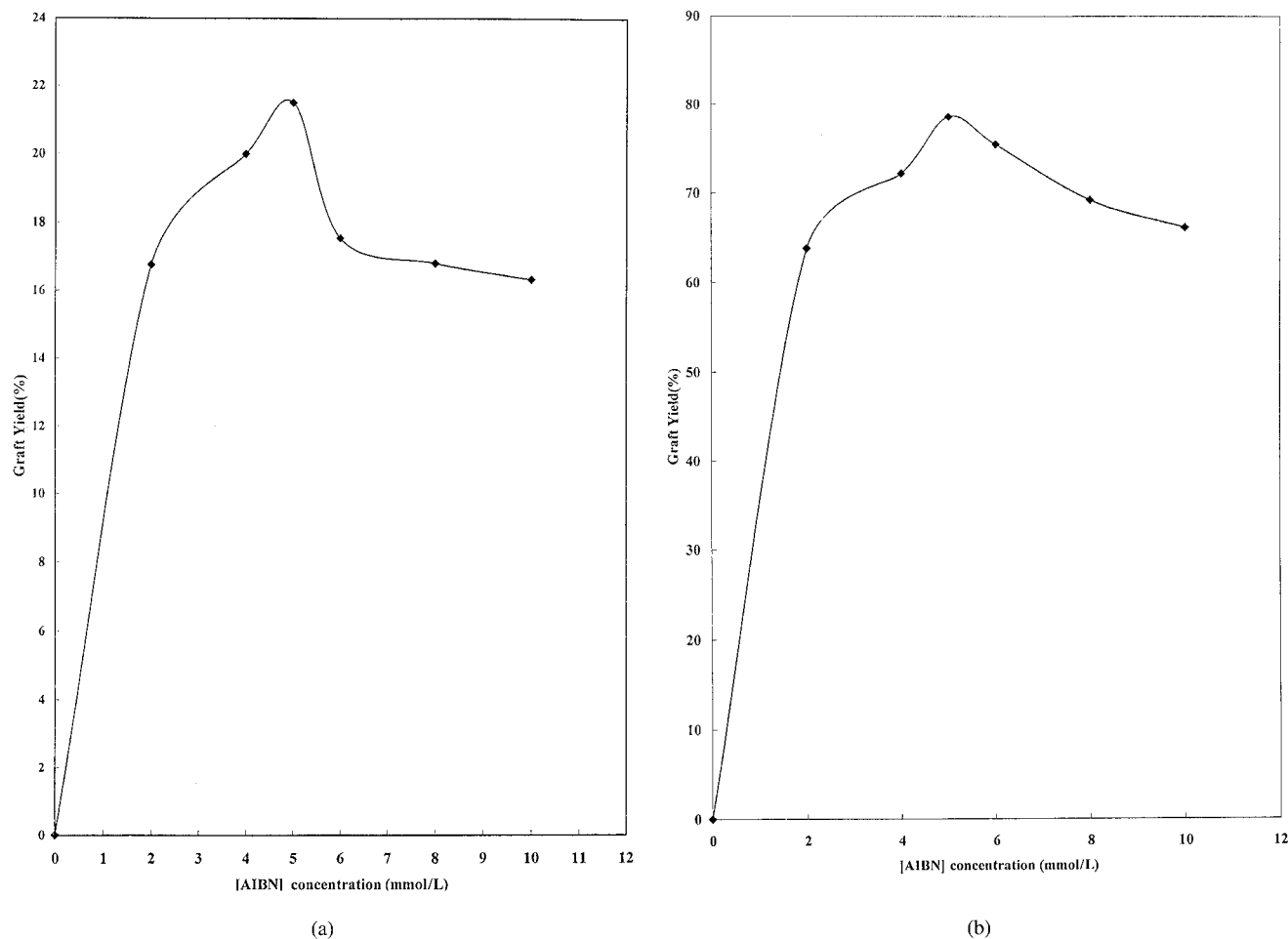
Figure 1 (a) Effect of AIBN concentration on percentage graft yield in the absence of activator. Conditions: [MMA], 8%; pH, 2; grafting time, 3 h; grafting temperature, 70°C; methanol : water ratio, 30 : 70; material : liquor ratio, 1 : 50. (b) Effect of AIBN concentration on percentage graft yield in the presence of activator. Conditions: [Fe^{2+}]; other conditions as in (a).

AIBN concentration

Figure 1(a) shows the dependency of the graft yield (%GY) on the concentration of AIBN (initiator) when graft polymerization of MMA onto cellulose thiocarbonate was performed using 8% MMA, at pH 2 and a temperature of 70°C for 3 h; a methanol/water ratio of 30 : 70 and maintaining the material/liquor ratio at 1 : 50. From Figure 1(a) it may be seen that as the AIBN concentration increases, there is an increase in percentage of grafting in the lower concentration range; it reaches a maximum value at an AIBN concentration of 5 mmol/L. Beyond this concentration, the graft yield decreases. This suggests that increasing the AIBN concentration to 5 mmol/L is accompanied by enlarging the generation of the cyanoisopropyl radicals [eq. (1)] and in turn the cellulose macroradicals capable of initiating grafting reaction along with the cellulose backbone. Nevertheless, at concentrations of AIBN higher than 5 mmol/L, the grafting solution would be repleted by the cyanoisopropyl radicals. That is, the cyanoiso-

propyl radicals tend to interact with each other to produce stable products [eqs. (2) and (3)].

Moreover, at higher initiator concentration, reactions that are competitive to grafting probably take place in solution (i.e., homopolymerization of MMA and termination of the growing polymer chains along with the cellulose backbone[26]).

Figure 1(b) shows the effect of AIBN concentration on the graft yield when MMA was grafted onto cotton fabric using the ferrous cellulose thiocarbonate–AIBN redox system. Concerning this, the cellulose thiocarbonate sample was pretreated with a freshly prepared solution of ferrous ammonium sulfate (0.1 mmol/L). The treated sample, referred to as ferrous cellulose thiocarbonate, was then grafted under the same conditions cited in Figure 1(a). The data of Figure 1(b) show a trend similar to that of Figure 1(a). However, it is clear [Fig. 1(b)] that incorporation of Fe^{2+} ions in the initiating system would greatly enhance the grafting reaction. This is because the Fe^{2+} ions are responsible for generation
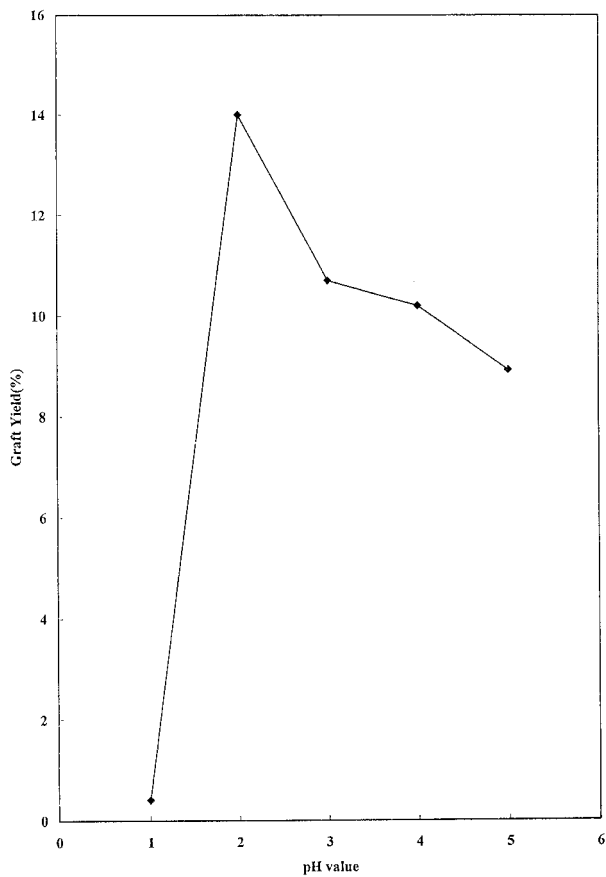
(a)
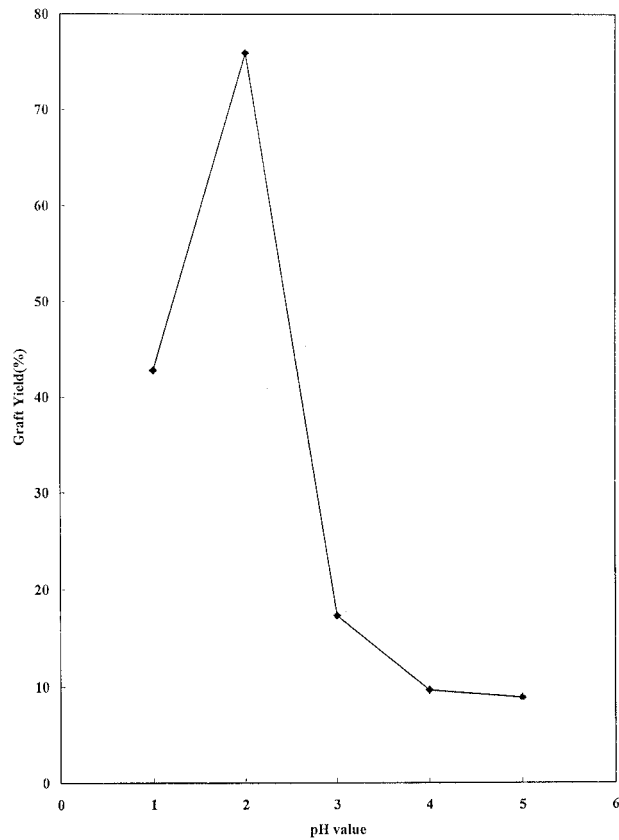
(b)
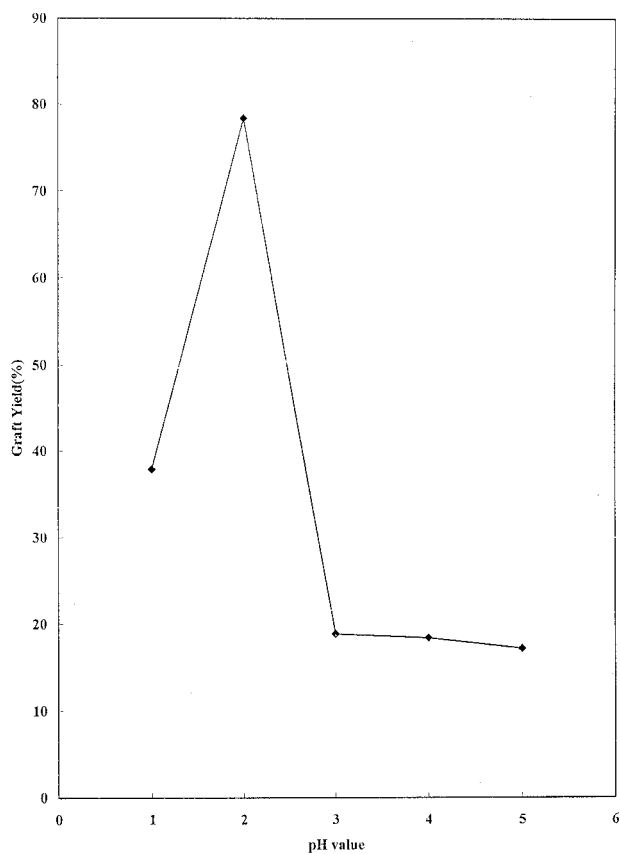
(c)

Figure 2   Effect of pH of the polymerization medium on the graft yield: (a) —◆—unmodified cellulose (blank) grafted in the absence of activator; (b) —◆—thiocarbonated cellulose grafted in the absence of activator; (c) —◆—thiocarbonated cellulose grafted in the presence of activator. Conditions for (a)–(c): [AIBN], 5 mmol/L; [MMA], 8%; grafting time, 3 h; grafting temperature, 70°C; methanol : water ratio, 30 : 70; material : liquor ratio, 1 : 50.

of excessive amounts of free radicals capable of initiating grafting of MMA onto cotton fabric, as already mentioned [eqs. (10)–(15)].

pH and nature of substrate

For comparison purposes, three different substrates—the untreated cotton cellulose (control), cellulose thiocarbonate, and ferrous cellulose thiocarbonate—were separately grafted with MMA (6%) by AIBN (5 mmol/L) at different pH values ranging from 1 to 5. The polymerization reaction was carried out at 70°C for 3 h using a methanol/water liquor ratio of 30 : 70 and a material/liquor ratio of 1 : 50. Figure 2(a)–(c) show the results obtained. A comparison between Figure 2(a), (b), and (c) indicates the following. (1) The graft yield increases significantly by changing the pH value to reach a maximum at pH 2. Higher pH values sharply decrease the graft yield. This holds true irrespective of the nature of the substrate used. (2) The three substrates have different abilities toward grafting with MMA. The graft yield follows the order: Fe^{2+}–cellulose thiocarbonate > cellulose–thiocarbonate $\gg$ untreated cellulose (control).

The considerable increments in the graft yield at pH $\leq$ 2 could be interpreted in terms of the favoring influence of the strongly acidic medium on the formation of the cellulose macroradicals and/or the cyanoisopropyl radicals. Stated in other words, at lower acidity, pH > 2, the rate of formation of these radicals may probably be suppressed.

The differences in graft yields between the untreated cellulose (control), cellulose thiocarbonate, and ferrous cellulose thiocarbonate would be expected to result from differences in their reducing capacities. Generally speaking, the substrate with the highest reducing capacity is the most suitable one to initiate grafting. This holds true with the ferrous cellulose thiocarbonate. The latter has the hydrosulfide groups (–SH) and ferrous ions (both are reductants) and therefore it reflects a maximum reducing capacity compared with that of the other two substrates. Logically, the weak covalent bonding between the S-atom and the H-atom greatly facilitates abstraction of hydrogen atoms from the hydrosulfide groups by the cycanoisopropyl radicals to form the cellulose thiocarbonate radicals (**X**) [eq. (4)[rsqb], which in turn rapidly disintegrate to form the most stable cellulose macroradicals (**XI**) [eq. (5)[rsqb]. Moreover, the presence of Fe^{2+} ions adsorbed onto the fabric surface would considerably facilitate the formation of active species capable of initiating grafting along with the fabric surface [eqs. (9)–(15)].

Because of the absence of Fe^{2+} ions, the cellulose thiocarbonate substrate imparts lower ability to be grafted with MMA compared with the ferrous cellulose thiocarbonate substrate.

On the other hand, the lowest tendency of the untreated cellulose (control) to be grafted with MMA is a logical consequence, given that it has the lowest reducing capacity. It is difficult for the H-atoms of the cellulose hydroxyls to be abstracted by the cyanoisopropyl radicals or by other active species generated in the polymerization medium, compared to the H-atoms of the (–SH) groups.
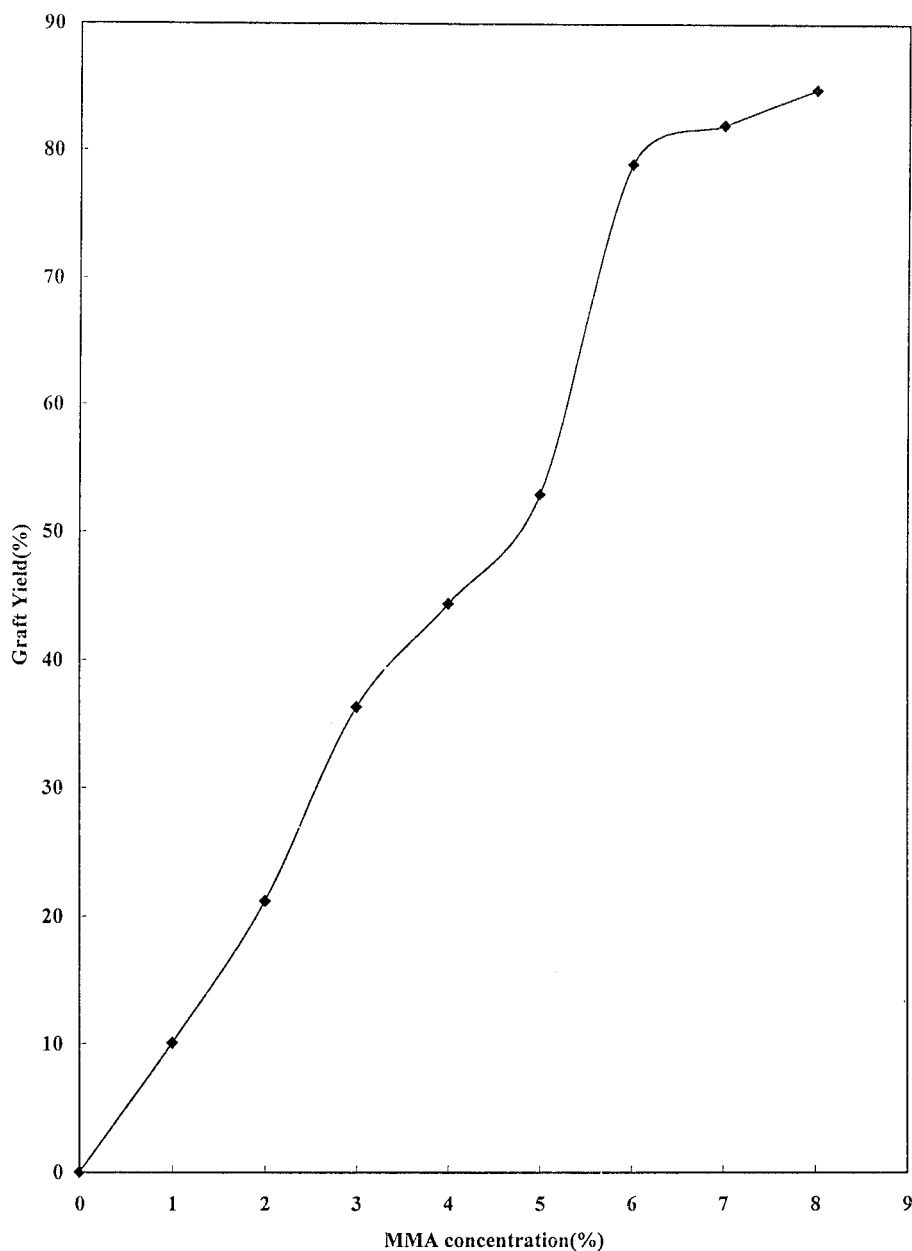
Monomer concentration

Figure 3 shows the graft yields obtained with the cotton fabric at different concentrations of MMA. It may be seen that the higher the concentration of MMA in the polymerization system, the higher the grafting.

The significant enhancement of grafting with the use of high monomer concentration could be associated with the favorable effect of the monomer concentration on producing a large number of growing polymer chains. This and the availability of the monomer in the vicinity of and/or inside the cellulose fabric would certainly facilitate grafting. In addition, the gel effect, which is brought about at high monomer concentration because of the solubility of poly(methyl methacrylate) in its own monomer, seems to play a significant role here. The role of the gel effect[27] is to promote grafting through hindrance of the termination of the growing polymer chain radicals by coupling as well as increasing the swellability of cotton cellulose. The effect of increasing the cellulose swellability is to assist diffusion of low molecular weight growing homopolymer chains to the interior of cellulose for a transfer reaction. It also facilitates diffusion of monomer to the growing grafted chains and active sites on the cellulose backbone, thereby leading to higher grafting.

Polymerization temperature

Figure 4 shows the rate of grafting of MMA on cellulose at three temperatures, 60, 70, and 80°C. It is evident that the rate of grafting is dependent on temperature, in the order: 70°C > 60°C > 80°C. This holds true after 1 h of the polymerization period, but before this time the grafting rate follows the order: 70°C > 80°C > 60°C. Thus, 70°C seems to be the optimum temperature for grafting of MMA onto cotton fabric using the ferrous cellulose thiocarbonate–AIBN redox initiation system. Although raising the temperature increases the efficiency of the said redox system and in turn enhances the rate of the grafting reaction,[28] it also favors the homopolymerization reaction that would account for the lower magnitude of grafting at 80 than at 70°C. Nevertheless, the contribution of a faster rate of termination at higher temperature in decreasing the graft yield cannot be ruled out.

Figure 3 Effect of MMA concentration on the graft yield in the presence of activator. Conditions: [AIBN], 5 mmol/L; [Fe^{2+}], 0.1 mmol/L; pH, 2; grafting time, 3 h; grafting temperature, 70°C; methanol : water ratio, 30 : 70; material : liquor ratio, 1 : 50.

Duration of polymerization

Figure 4 shows that the rate of grafting is characterized by an initial fast rate followed by a slower rate. This is observed irrespective of the polymerization temperature applied. The slower rate of polymerization reactions could be associated with depletion in AIBN and MMA concentrations as well as reduction in available sites for grafting on the cellulose backbone, as the reaction proceeds.

Nature of monomer

The ability of the ferrous cellulose thiocarbonate–AIBN redox initiation system for inducing grafting of

methly acrylate (MA), acrylonitrile (AN), and acrylic acid (AA) onto cotton fabric may be realized from the data depicted in Figure 5. Results of the graft yields obtained with MMA are also given in the same figure for comparison. It is obvious that, with a given monomer concentration, MMA shows the highest reactivity for grafting onto cotton cellulose compared with other acrylic monomers. The graft yield is in the order: MMA $\gg$ AA > MA $\approx$ AN.

The differences in the behavior of the monomers will depend on such factors as relative tendency to activation, the ability of the monomer molecules to convert to free radicals, the ability of the monomer radicals to graft and/or homopolymerize, the ability
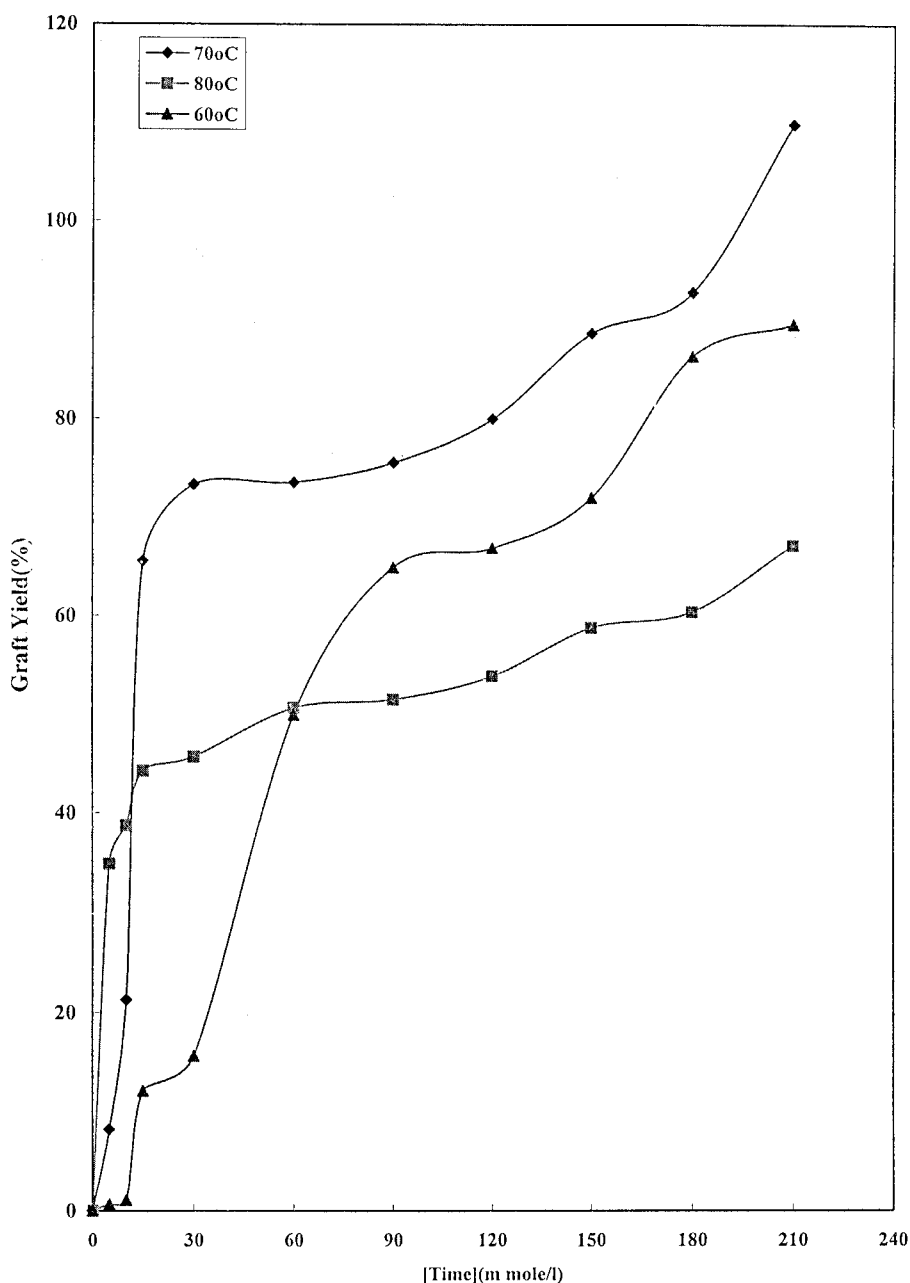
Figure 4 Influence of polymerization time on the graft yield in the presence of activator at different temperatures. Conditions: [AIBN], 5 mmol/L; [MMA], 8%; [Fe^{2+}], 0.1 mmol/L; pH, 2; methanol : water ratio, 30 : 70; material : liquor ratio, 1 : 50.

of these radicals to complexate with the substrate, molecular size, and the miscibility and diffusion of the monomer molecule and/or its radical from the aqueous phase to the fiber phase.

Reaction medium

Grafting of MMA onto cotton fabric using the ferrous cellulose thiocarbonate–AIBN redox system was carried out in solvent/water mixtures, at different ratios. Solvents used included: methanol, isopropanol, 1,4-dioxane, cyclohexane, benzene, DMF, and DMSO. The

results obtained, shown in Figure 6, provide evidence that (1) the nature and ratio of solvent in the reaction medium determine the magnitude of grafting; (2) methanol is superior to other solvents, given that it brings about, in most instances, graft yields higher than those obtained with the other solvents. The highest graft yield was obtained when the methanol/water ratio of 30 : 70 was used; (3) benzene, as an aromatic solvent, brings about the lowest graft yields compared to those of the aliphatic solvents examined; and (4) the solvent/water ratio of 5 : 95 constitutes the most favorable medium for most solvents under investigation
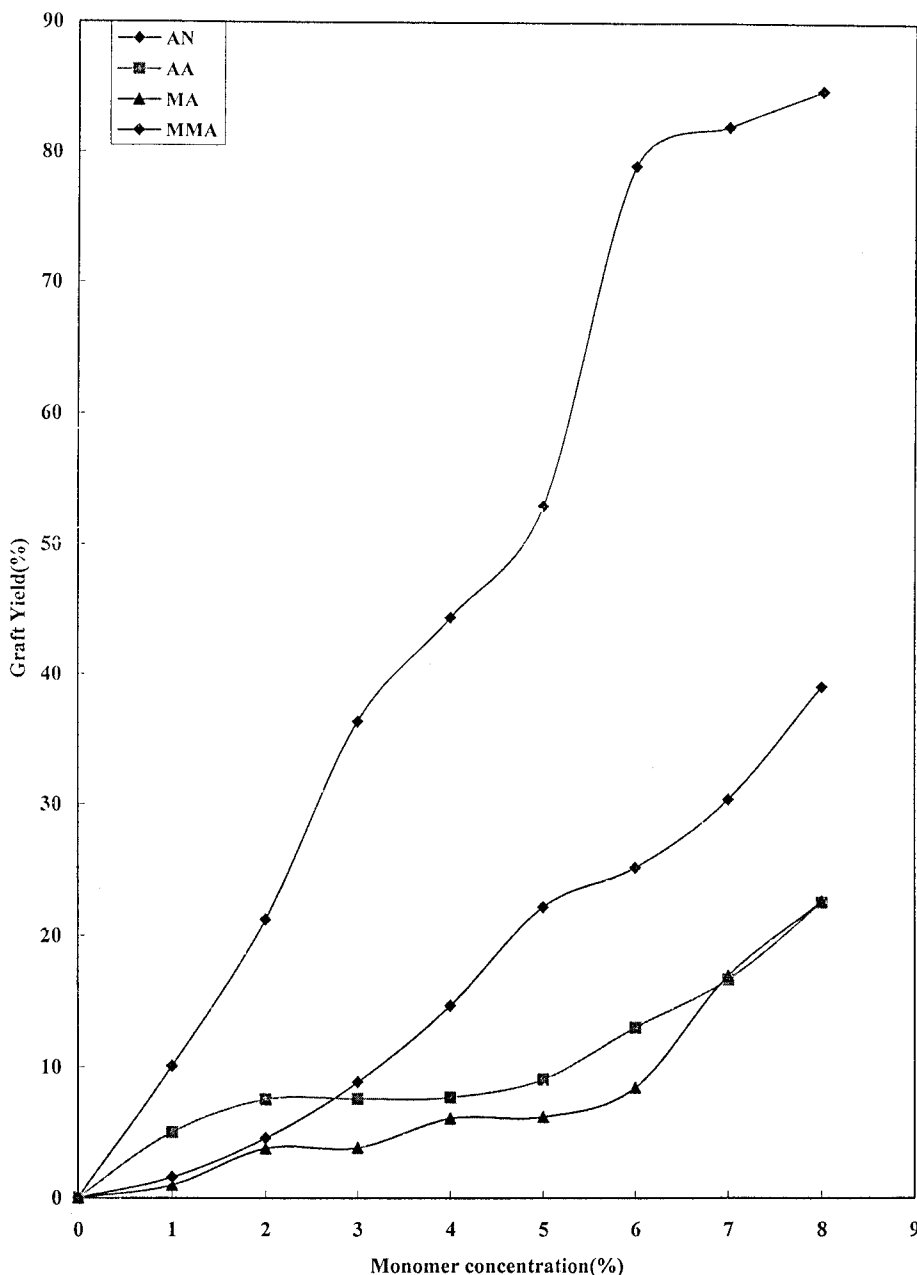
Figure 5 Dependency of the graft yield on the nature of vinyl monomer in the presence of activator. Conditions: [AIBN], 5 mmol/L; [Fe²⁺], 0.1 mmol/L; pH, 2; grafting time, 3 h; grafting temperature, 70°C; methanol : water ratio, 30 : 70; material : liquor ratio, 1 : 50.

for grafting MMA onto cotton cellulose by using the ferrous cellulose thiocarbonate–AIBN redox system. For the optimum solvent/water ratio of 5 : 95, the graft yield follows the order: methanol > DMF > iso-propanol > DMSO > cyclohexane > 1,4-dioxane > benzene.

Differences in the magnitude of grafting by nature and concentration of the solvent may be associated with differences in the ability of the solvent with respect to:

1. Miscibility of the monomer.
2. Formation of solvent radical and/or hydrogen or hydroxyl radicals from water under the in-

fluence of primary radical species of the initiating system.
3. Contribution of the solvent radical in formation of cellulose macroradicals.
4. Swelling of the fibers that favors diffusion of the monomer more toward the grafting site.
5. Termination of the growing grafted chains by chain-transfer reactions.

The first four factors favor grafting; the last factor lowers it.[29]
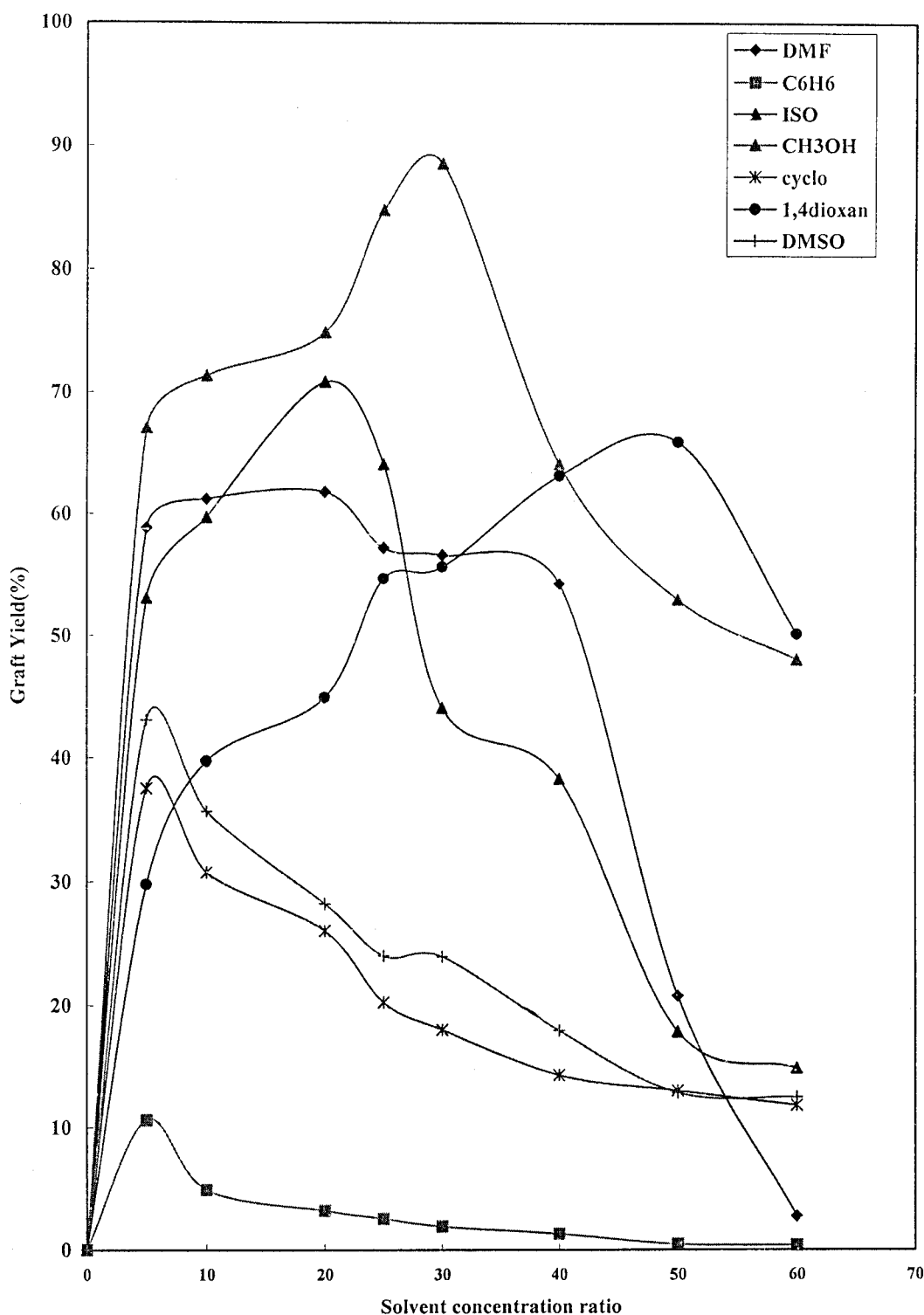
Figure 6 Effect of the polymerization medium on the graft yield in the presence of activator. Conditions: [AIBN], 5 mmol/L; [MMA], 8%; [Fe^{2+}], 0.1 mmol/L; pH, 2; grafting time, 3 h; grafting temperature, 70°C; material : liquor ratio, 1 : 50.
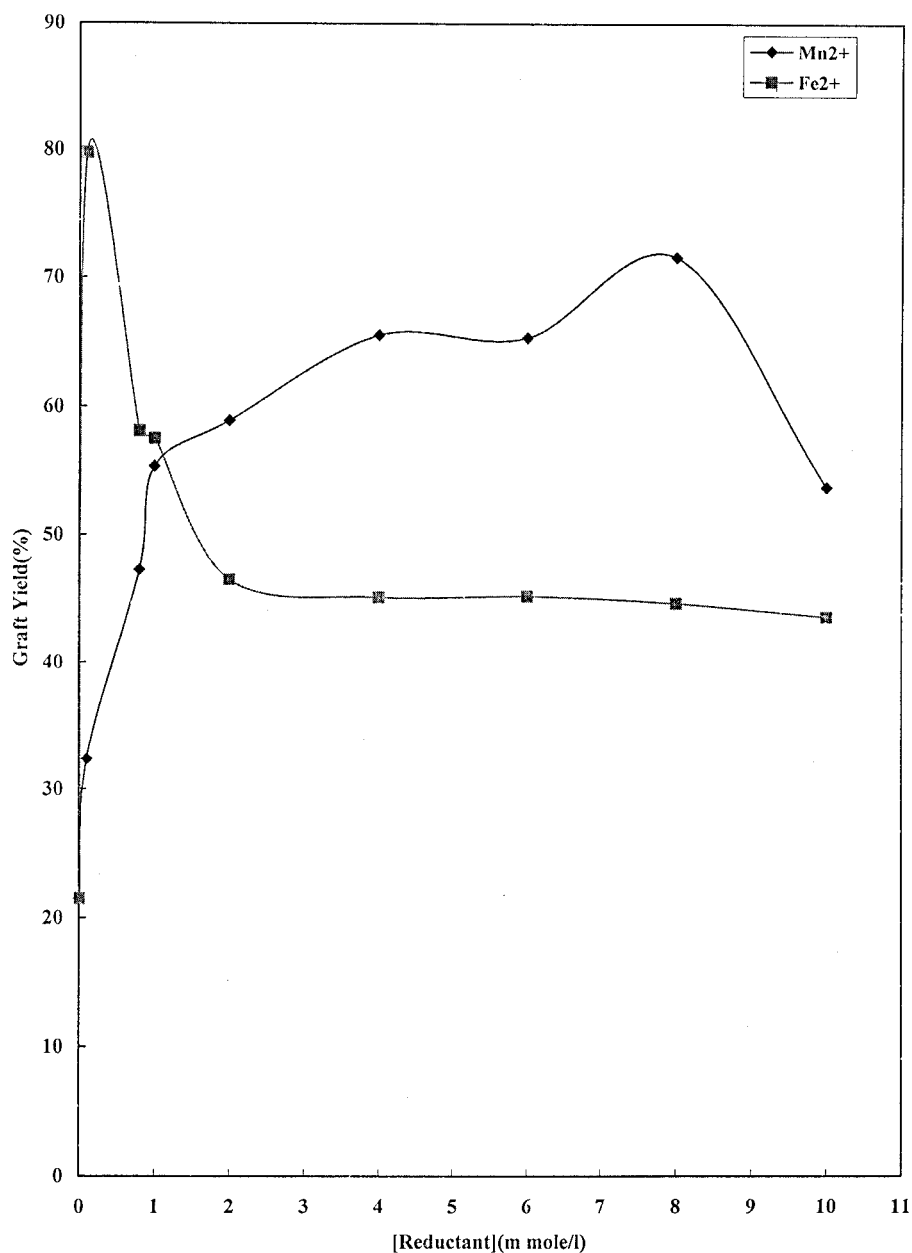
Effect of metallic ion

Effect of metal-ion reductants

In the foregoing sections, all the polymerization reactions were carried out by incorporating Fe^{2+} ion as an activator for the cellulose thiocarbonate–AIBN system.

Incorporation of Fe^{2+} ions in the cited initiation system would greatly heighten the grafting reaction. For comparison purposes, experiments were made to examine another reductant, manganous sulfate.

The cellulose thiocarbonate fabric was treated with different concentrations of a solution containing man-
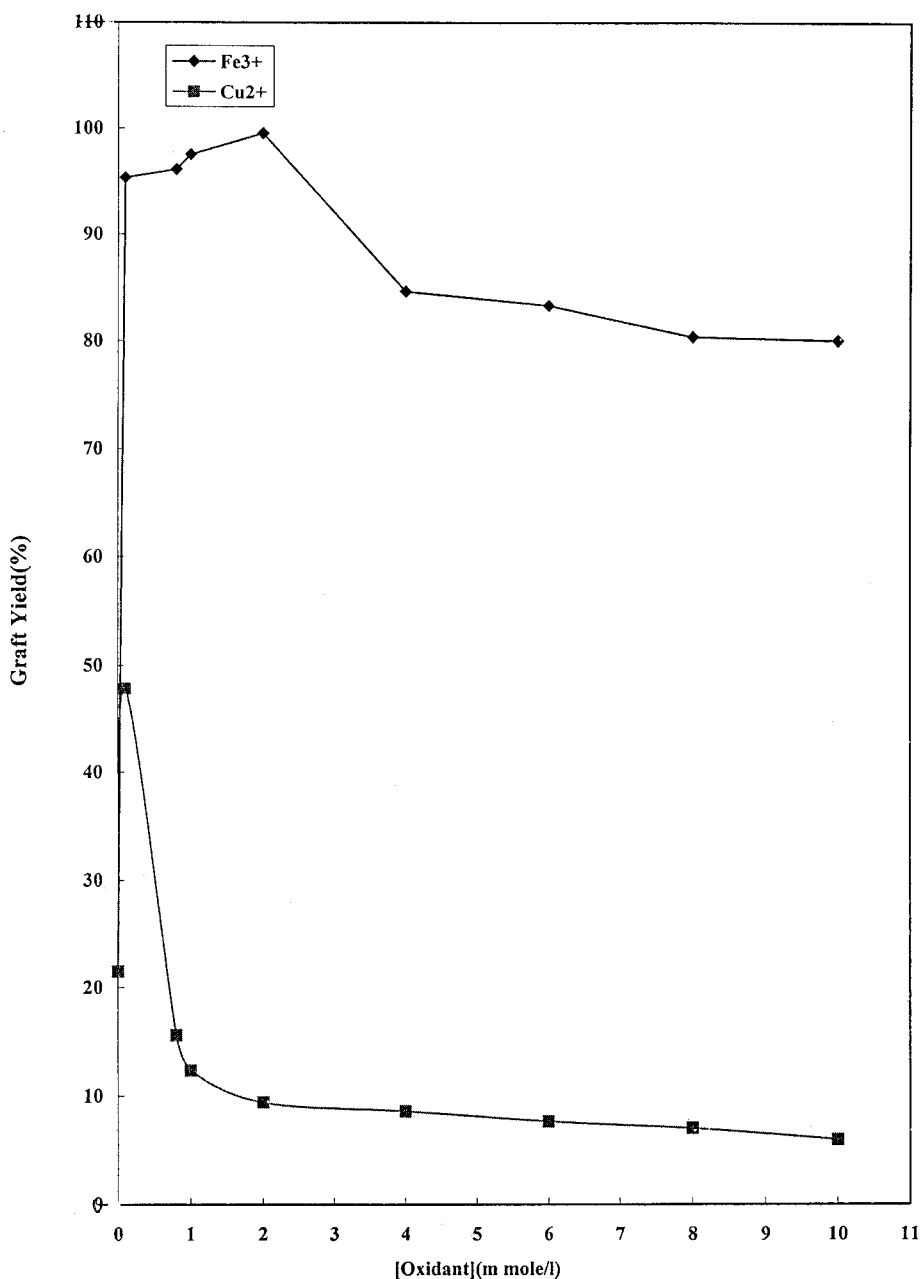
Figure 7   Effect of metal-ion reductants on the graft yield. Conditions: [AIBN], 5 mmol/L; [MMA], 8%; pH, 2; grafting time, 3 h; grafting temperature, 70°C; methanol : water ratio, 30 : 70; material : liquor ratio, 1 : 50.

ganous ions as described in detail in the experimental section. The metallized cellulose thiocarbonate fabric so obtained was grafted with MMA (8%) using AIBN (5 mmol/L). The polymerization was conducted at 70°C and pH 2, keeping the methanol/water ratio of 30 : 70 and material/liquor ratio of 1 : 50. The results obtained are shown in Figure 7. For comparison, results of Fe^{2+} ion are also given in the same figure.

The data of Figure 7 clearly reveal the following. (1) The presence of a metal-ion reductant on the fabric surface increases the grafting efficiency, regardless of the nature of the reductant used. (2) The ferrous cellulose thiocarbonate fabric imparts the highest graft yield at the lowest Fe^{2+} concentration (i.e., 0.1 mmol/L) over those obtained with the manganous cellulose thiocarbonate fabric at the same concentration. Further increases in the Fe^{2+} ion concentration bring about decrements in the magnitude of grafting up to 2 mmol/L, after which it levels off. (3) Increasing the concentrations of Mn^{2+} on the fabric surface causes the magnitude of grafting to increase and reach a maximum at a concentration of 8 mmol/L, beyond which concentration the grafting decreases.

The aforementioned results may be explained in terms of the efficiency of each metal-ion reductant:

Figure 8 Effect of metal-ion oxidant on the graft yield. Conditions: [AIBN], 5 mmol/L; [MMA], 8%; pH, 2; grafting time, 3 h; grafting temperature, 70°C; methanol : water ratio, 30 : 70; material : liquor ratio, 1 : 50.

1. To enhance decomposition of AIBN to the cyanoisopropyl radicals.[30]
2. To autocatalyze the initiating system.[31,32]
3. To terminate the grafting reaction.

The first two factors are responsible for enhancement in the graft percentage. The last factor, operating at high metal ion concentration, lowers the graft percentage.

Effect of metal-ion oxidants

The metal-ion oxidants ferric ammonium sulfate and copper sulfate were individually incorporated in the grafting solution containing the cellulose thiocarbonate fabric (Fig. 8). The latter was grafted with MMA under the graft conditions cited in Figure 7. The data of Figure 8 disclose that:

1. Incorporation of Fe^{3+} ions in the polymerization system brings about maximum graft yields with the concentrations range of 0.1–2 mmol/L. Beyond this, the graft yield decreases.
2. The optimum graft yield is obtained when 0.1 mmol/L copper sulfate was used.
3. At any event, the graft yield obtained with Fe^{3+} ion was superior to that obtained with Cu^{2+} ion.

The above findings could be clarified in terms of the roles played by the metal-ion oxidants during the polymerization reactions. It is reasonable to recognize that the oxidants, in the current work, are characterized by different chemical features; that is, they act both as free-radical generators [eqs. (11)–(15)][24] and as chain terminators, particularly at higher concentrations.[7,33,34] The preeminence of one feature over another would explain the difference in the behavior of the graft yield with increasing the metal-ion oxidant concentration in the polymerization medium.

References

1. Bando, Y.; Minoura, Y. J Polym Sci Polym Chem Ed 1976, 14, 693.
2. Musnev, O. N.; Babaev, T. M.; Karimov, V. A.; Azimov, A. A.; Tillaev, R. S.; Usmanov, Kh. U. Nceuchn Tr-Teshk Gos Univ 1976, 502, 33.
3. Tsubokawa, N.; Kimoto, T.; Koyama, K. Colloid Polym Sci 1993, 271, 940.
4. Pollack, S. K.; Narayanswamy, B.; Macomber, R. S.; Rardon, D. E.; Constantunides, I. Macromolecules 1993, 26, 856.
5. Fernandez-Monreal, M. C.; Cuervo, R.; Madruga, E. L. J Polym Sci Part A: Polym Chem 1992, 30, 2313.
6. Nguyen, C.; Zavarin, E. J Appl Polym Sci 1992, 46, 1103.
7. El-Rafie, M. H.; Khalil, M. I.; Hebeish, A. J Appl Polym Sci 1975, 19, 1677.
8. Hebeish, A.; Khalil, M. I.; El-Rafie, M. H. Angew Makromol Chem 1974, 37, 149.
9. Sankholkar, S.; Deb, P. C. J Appl Polym Sci 1990, 39, 1681.
10. Takahashi, A.; Sugahara, Y.; Hirano, Y. J Polym Sci Part A: Polym Chem 1989, 27, 3817.
11. Nomura, M.; Ikama, J.; Fujita, K. J Polym Sci Part A: Polym Chem 1993, 31, 2103.
12. Hebeish, A.; Bendak, A.; Kantouch, A. J Appl Polym Sci 1971, 15, 2733.
13. El-Rafie, M. H.; Khalil, E. M.; Zahran, M. K.; Hebeish, A. Cellul Chem Technol 1989, 23, 683.
14. Bickel, A. F.; Waters, W. A. Recl Trav Chim Pays-Bas 1950, 69, 1490.
15. Bawn, C. R. M.; Mellish, S. F. Trans Faraday Soc 1951, 47, 1216.
16. Lewis, F. M.; Matheson, M. S. J Am Chem Soc 1949, 71, 747.
17. Aruett, L. M. J Am Chem Soc 1952, 74, 2027.
18. Overberger, C. G.; Biletch, H. J Am Chem Soc 1951, 73, 4880.
19. Talat-Erben, M.; Bywater, S. J Am Chem Soc 1955, 77, 3710.
20. Hammond, G. S.; Trapp, O. B.; Keys, O. T.; Neff, D. L. J Am Chem Soc 1959, 81, 4878.
21. Talat-Erben, M.; Isfendiyaroglu, A. N. Can J Chem 1958, 36, 1156.
22. Smith, P.; Carbone, S. J Am Chem Soc 1959, 81, 6174.
23. Talat-Erben, M.; Bywater, S. J Am Chem Soc 1959, 77, 3712.
24. El-Rafie, M. H.; Zahran, M. K.; Hebeish, A. Polym Degrad Stab 1993, 42, 223.
25. Waters, W. A. Mechanisms of Oxidation of Organic Compounds; Spottiswoode Ballantyne and Co.: London/Colchester, 1964; p. 36.
26. Khalil, E. M.; El-Rafie, M. H.; Zahran, M. K.; Hebeish, A. Cellul Chem Technol 1990, 24, 65.
27. Bendak, A.; Hebeish A. J Appl Polym Sci 1973, 17, 1953.
28. Waly, A.; Hebeish, A.; Zahran, M. K.; El-zairy, M. R.; Rashad, M. Polym Compos 1995, 3, 1.
29. Hebeish, A.; El-Rafie, M. H.; Zahran, M. K. J Appl Polym Sci 1993, 50, 2099.
30. Benson, D. Mechanisms of Oxidation by Metal Ions; Elsevier Scientific: Amesterdam, 1976; p. 132.
31. Palit, S. R.; Konar, R. S. J Polym Sci 1962, 58, 85.
32. Tripathy, S. S.; Jena, S.; Misra, S. B.; Padhi, N. P.; Singh, B. C. J Appl Polym Sci 1985, 30, 1399.
33. Narita, H.; Sakamoto, Y.; Machida, S. Makromol Chem 1972, 152, 143.
34. Collinson, E.; Dainton, F. S.; McNaughton, G. S. Trans Faraday Soc 1957, 53, 489.