

Grafting of Methacrylic Acid to Loomstate Viscose Fabric Using $\text{KMnO}_4/\text{NaClO}_2$ System

S. A. ABDEL HAFIZ,* M. H. EL-RAFIE, S. M. HASSAN, and A. HEBEISH†

National Research Centre, Textile Research Division, Dokki, Cairo, Egypt

SYNOPSIS

Graft polymerization of methacrylic acid (MAA) to loomstate viscose fabric (greige fabric) using $\text{KMnO}_4/\text{NaClO}_2$ system was studied. Residual thiocarbonate and/or sizing materials on the fabric as well as presence of NaClO_2 act in favor of primary radical formation which, in turn, accelerate formation of cellulose macroradicals capable of initiating grafting. The polymerization reaction was studied with respect to polymer yield, graft yield, homopolymer, total conversion, and graft efficiency. The magnitude of each of these characteristics was found to depend upon parameters such as concentrations of KMnO_4 , NaClO_2 , and MAA as well as liquor ratio, reaction time, and temperature of polymerization. By and large all these parameters enhance the polymerization process with the exception of the liquor ratio. A reaction mechanism for the polymerization reaction is also reported. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Grafting of cellulose and cellulose derivatives with various synthetic polymers has been extensively studied and reviewed by Hebeish and Guthrie.¹ Many different methods of grafting have been developed.²⁻²² In most methods, radicals are generated along the cellulose backbone in the presence of vinyl monomers that may be polymerized by these radicals. One disadvantage in these grafting procedures is the formation of considerable amounts of homopolymer, which may be difficult to remove from the copolymer.

Detailed studies onto cotton fabrics using cellulose thiocarbonate-oxidant redox system were also reported. Oxidant used include hydrogen peroxide,²³ potassium permanganate,²⁴ hexavalent chromium ion,²⁵ potassium persulfate,²⁶ potassium bromate,^{27,28} pentavalent vanadium ion,²⁹ and ferric nitrate.³⁰

Recently, we have developed conditions for vinyl graft copolymerization onto cotton fabric with very

little or no homopolymer formation. This system is based on utilization of loomstate cotton fabric the warps of which are sized with starch, methacrylic acid as the monomer, and KMnO_4 /citric acid as initiator.³¹

It is expected that loomstate viscose fabric (greige fabric) contains residual thiocarbonate groups that helps the deposition of MnO_2 over the fabric. These findings stimulated the present work, which aims to develop an improved condition for vinyl graft copolymerization onto viscose fabric. The system involves utilization of loomstate viscose fabric along with KMnO_4 , NaClO_2 , and methacrylic acid. The polymerization reaction was carried out at different conditions including initiator concentration, liquor ratio, duration, and temperature of polymerization as well as studied with respect to graft yield, homopolymer, total conversion, and graft efficiency.

EXPERIMENTAL

Materials

Loomstate viscose plain weave (51 picks and 21 ends/cm) fabric (greige fabric) was used as received from the mill. Methacrylic acid (MAA) was used without further purification. Nonionic wetting

* Present address: Helwan University, Faculty of Science, Chemistry Department, Cairo, Egypt.

† To whom correspondence should be addressed.

agent, namely Nonidet LE, was kindly supplied by Shell Textile Chemicals, Cairo, Egypt. Potassium permanganate and sodium chlorite were of reagent-grade chemicals.

Procedures

Unless otherwise indicated, treatment of loomstate viscose fabric (greige fabric) with KMnO_4 and grafting of the so treated fabric were carried out as described below.

Treatment with KMnO_4

The loomstate viscose fabric (greige fabric) was impregnated in an aqueous solution containing specific concentration of KMnO_4 and 2 g/L nonionic wetting agent. The treatment was carried out at 50°C for 15 min using a material-to-liquor ratio 1 : 30 with continuous shaking to avoid the heterogeneity of MnO_2 deposition on the fabric surface. After this treatment the fabric was thoroughly washed with water squeezed between two papers before immersing in the polymerization solution.

Graft Polymerization

The so obtained KMnO_4 -treated viscose was introduced in a 100-mL stoppered conical flask containing an aqueous solution of vinyl monomer and sodium chlorite. Material-to-liquor ratio 1 : 50 was used. Details of the reaction conditions are given in the text. At the end of the reaction, the sample was removed, thoroughly washed several times with cold and boiled water, and dried at 105°C for 3 h, then cooled over P_2O_5 for 2 h.

ANALYSIS

Percentage graft yield (%GY) was calculated as follows:

$$\%GY = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 is the dry weight of original sample and W_2 is the dry weight of the grafted sample. Percentage of total conversion (%TC), graft efficiency (%GE), and homopolymer (%H) were estimated by determination of the double bonds before and after polymerization of MAA according to a reported method.^{32,33} The standard iodine double-bond determination was modified as follows:

A 5-mL solution of MAA, containing about 4%

MAA, was transferred into a 500-mL iodine flask. To this solution was added 25 mL 0.2N bromate-bromide solution (containing 5.58 g of potassium bromate and 20 g of potassium bromide per liter) and 10 mL of 2N sulfuric acid. To avoid losses of bromine, pressure in the iodine flask was reduced slightly by cooling, so that the reagents were sucked into the flask. The solution was left to stand in the dark for 20 min and shaken frequently. Then 25 mL of 20% potassium iodide was added by the same suction technique. The iodine was then titrated with standard thiosulfate. A blank determination was also made.

$$\%TC = \frac{X_0 - X_1}{X_0} \times 100$$

$$\%GE = \frac{X_2}{X_0 - X_1} \times 100$$

$$\%H = \frac{X_0 - X_1 - X_2}{X_0} \times 100$$

where X_0 , X_1 , and X_2 are weight of blank monomer, weight of residual monomer, and weight of grafted monomer, respectively.

RESULTS AND DISCUSSION

In order to study grafting MAA onto viscose fabric (greige fabric) using potassium permanganate-sodium chlorite redox system, the graft polymerization reaction was carried out under different conditions. Variables studied include concentrations of potassium permanganate, sodium chlorite, and MAA (monomer), liquor ratio, as well as duration and temperature of polymerization. However, before going into detailed investigation of these parameters, it may be of importance as a start to shed some insight on the mechanism involved in grafting using the said initiation system.

Tentative Mechanism

When the viscose sample was impregnated in the potassium permanganate solution, it turned to brownish dark to black color of MnO_2 , depending on the concentration of the permanganate solution. Determination of the MnO_2 content of the sample revealed that the MnO_2 content increases substantially by increasing the concentration of KMnO_4 solution within the range studied as shown in Figure 1.

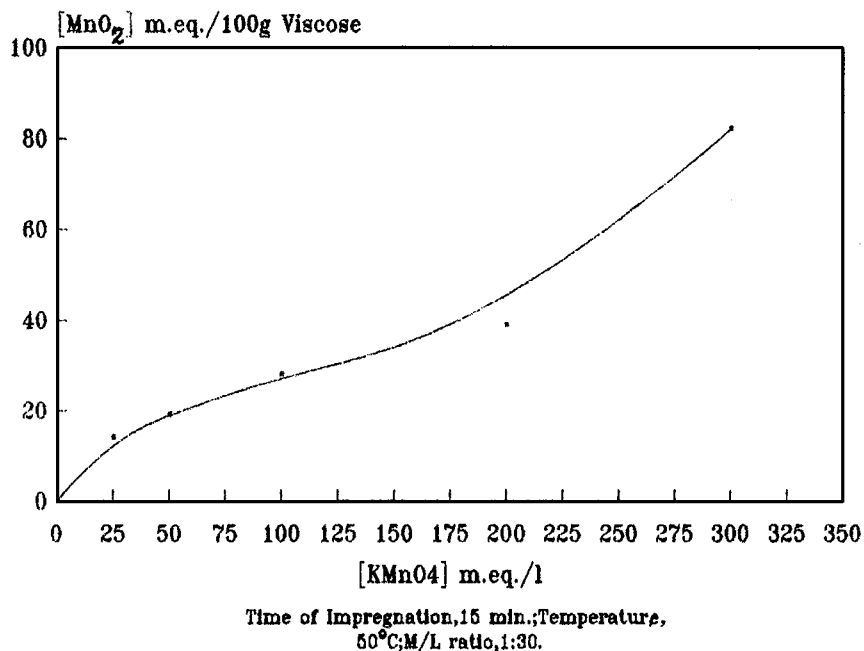
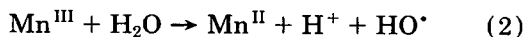
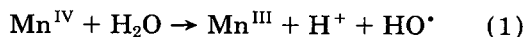
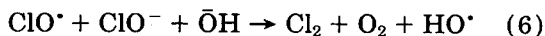
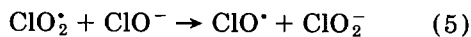


Figure 1 Effect of KMnO_4 concentration on the deposition of MnO_2 all over the viscose fabric surface. Time of impregnation, 15 min; temperature 50°C, M/L ratio, 1 : 30.

Mn^{IV} produces free radical species through reduction of Mn^{IV} to either Mn^{III} or Mn^{II} as suggested by Eqs. (1) and (2).²⁴



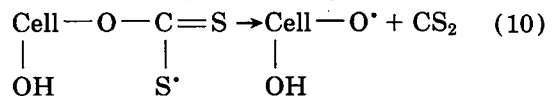
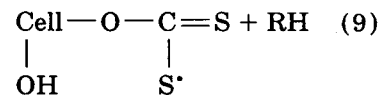
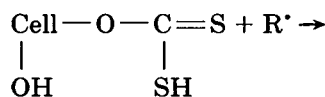
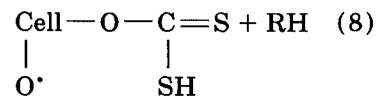
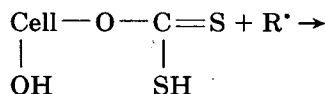
The hydroxyl free radical activates the chlorite ion and as a result a chain is perpetuated as exemplified by Eqs. (3)–(6).



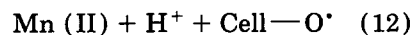
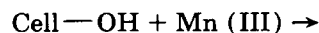
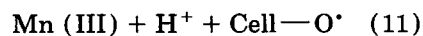
Once these free radical species (R^{\cdot}) are created, they produce cellulose macroradicals via direct abstraction of hydrogen atom from the hydroxyl groups of the cellulose as shown by Eq. (7).



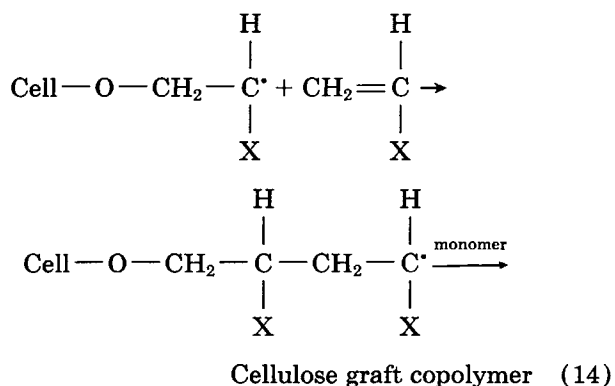
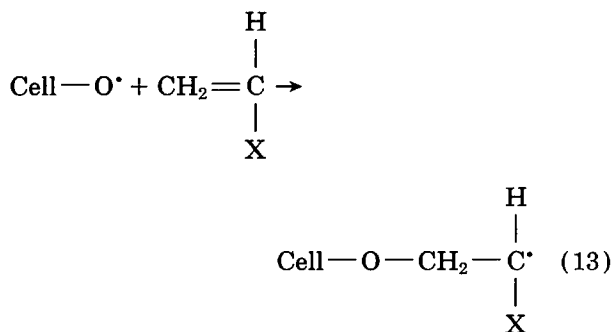
It is also likely that cellulose macroradicals are formed through disintegration of the residual cellulose thiocarbonate groups as suggested by the reaction scheme of Eqs. (8)–(10):



Furthermore cellulose macroradicals may also be formed upon direct attack of Mn^{IV} or Mn^{III} ions on the cellulose molecule, via abstraction of hydrogen atoms as suggested by Eqs. (11) and (12).



In the presence of vinyl monomers, the cellulose macroradical is added to the double bond of the vinyl monomer resulting in a covalent bond between the monomer and the cellulose with creation of a free radical on the monomer, i.e., a chain is initiated [Eq. (13)]. Subsequent addition of monomer molecules to the initiated chain propagates grafting onto cellulose [Eq. (14)].



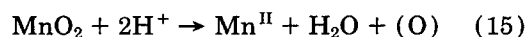
Potassium Permanganate Concentration

Figure 2 shows the effect of KMnO_4 concentration on percentages polymer yield. It is seen that the graft yield increases significantly by increasing the KMnO_4 up to 0.2N then decreases as the concentration of KMnO_4 further increases. The same holds true for total conversion and graft efficiency. On the other hand, the magnitude of homopolymer increases slightly by increasing the KMnO_4 .

The enhancement in grafting by increasing KMnO_4 concentration signifies the necessity of the presence of certain amount of deposited MnO_2 on the viscose fabric to act there upon to produce ultimately cellulose macroradicals capable of initiating grafting. On the other hand, decrement in grafting after 0.2N may be explained as follows:

As KMnO_4 increases, the deposition of MnO_2 within the viscose fabric increases and the diffusion rate of monomer is retarded by the excess deposition

of MnO_2 colloid particles. As a consequence of excess Mn^{IV} present, the oxidation of cellulose macromolecules and termination reactions would be intensified. It is also logical that higher amounts of inhibiting oxygen are produced at higher MnO_2 concentration due to the side reaction shown by Eq. (15).



Sodium Chlorite Concentration

Figure 3 shows the effect of sodium chlorite concentration on the percentages polymer yield when viscose- MnO_2 - NaClO_2 redox system was used to induce grafting of MAA onto viscose fabric. Obviously incorporation of NaClO_2 in the polymerization medium enhances the polymerization reaction provided that NaClO_2 concentration does not exceed a certain limit. The graft yield increases by increasing the chlorite concentration up to 0.2 mmol/L then decreases. The same situation is encountered with total conversion and graft efficiency. The homopolymer, on the other hand, tends to increase by increasing NaClO_2 concentration within the range studied.

The enhancement in the polymer yield by increasing NaClO_2 concentration up to 0.2 mmol/L is perhaps due to generation of extra primary free radical species as shown by Eqs. (3)–(6). The tendency of the polymer yield to decrease upon using higher NaClO_2 concentration could be ascribed to faster rate of termination because of abundance of primary free radical species and/or liberation of inhibiting oxygen [Eqs. (8) and (15)].

Liquor Ratio

Figure 4 shows the effect of liquor ratio on the percentages polymer yield. It is seen that the polymer yield (graft yield, homopolymer, total conversion, and graft efficiency) decreases as the liquor ratio increases within the range studied.

The decrease in the polymer yield could be attributed to (a) dilution of the polymerization medium due to the increase in the liquor ratio and as a result, the number of monomer and initiator molecules in the vicinity of the cellulose structure would decrease and (b) decrease in the rate of diffusion of monomer and initiator molecules from the aqueous phase to the fiber phase.

Monomer Concentration

Figure 5 shows the effect of MAA concentration on the percent polymer yield. It is seen that the graft

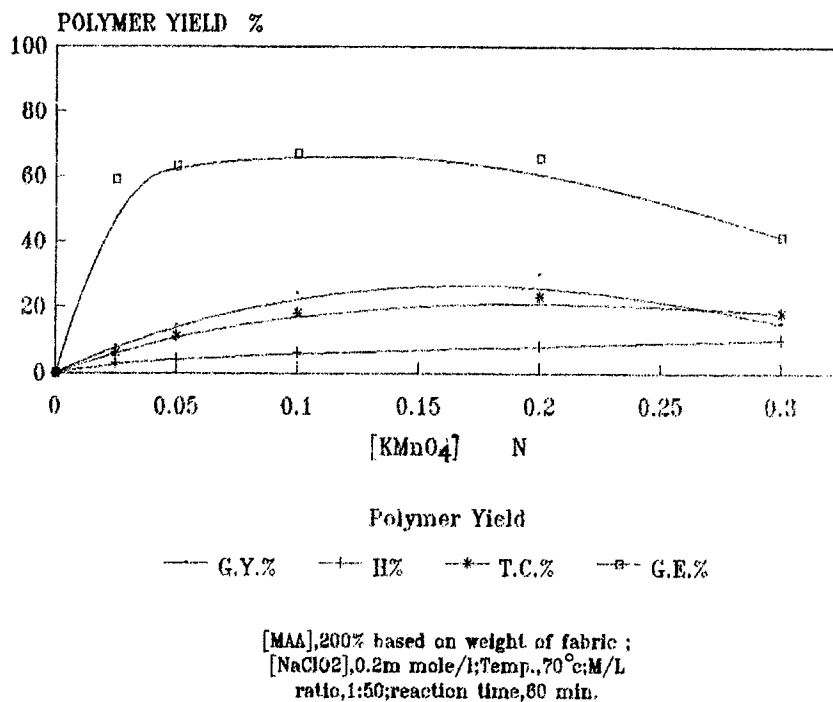


Figure 2 Potassium permanganate concentration vs. % polymer yield. (●) %GY; (+) %H; (*) %TC; (□) %GE; [MAA] 200% based on weight of fabric; [NaClO₂] 0.2 mmol/l; Temp., 70°C; M/L ratio 1 : 50; reaction time 60 min.

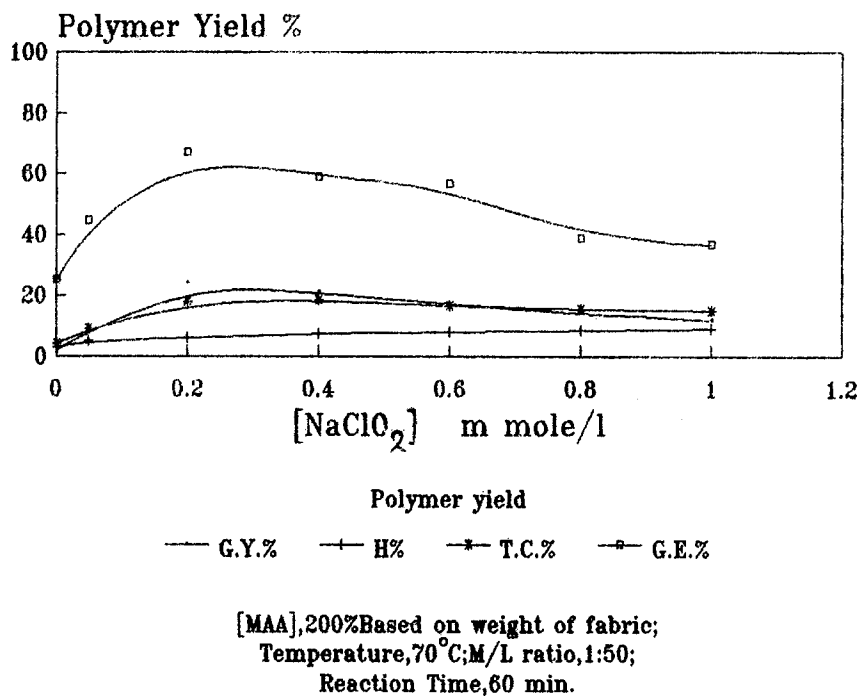
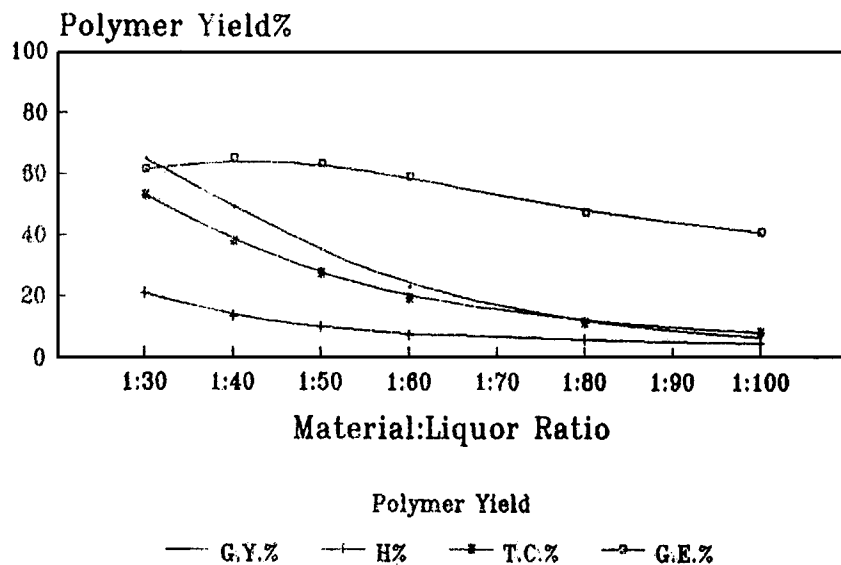
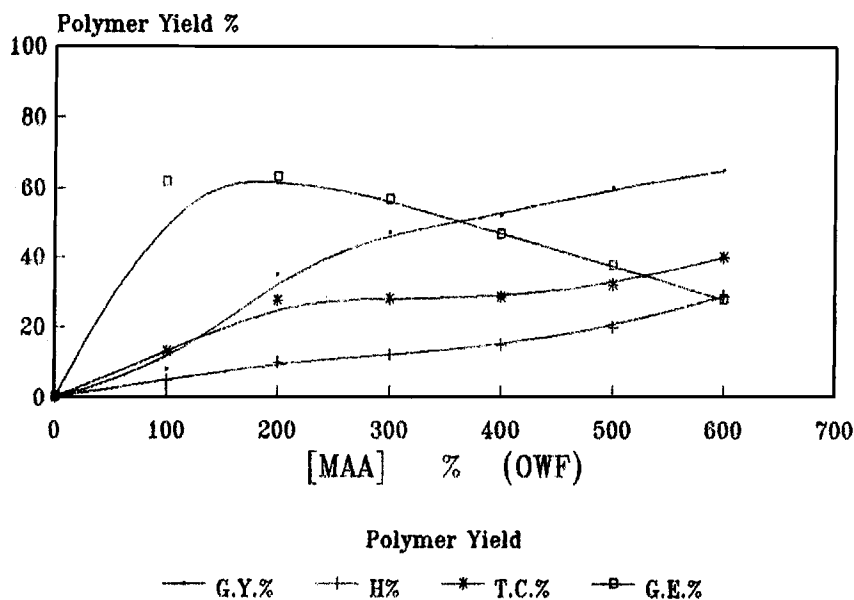


Figure 3 Sodium chloride concentration vs. percent polymer yield. (●) %GY; (+) %H; (*) %TC; (□) %GE; [MAA] 200% based on weight of fabric; Temp. 70°C; M/L ratio, 1 : 50; reaction time 60 min.



[MAA],200%Based on weight of fabric;
[NaClO₂],0.2 m mole/l;Temperature,70 C;
Reaction Time,90 min.

Figure 4 Liquor ratio vs. % polymer yield. (●) %GY; (+) %H; (*) %TC; (□) %GE; [MAA] 200% based on weight of fabric; [NaClO₂] 0.2 mmol/l; Temp., 70°C; reaction time, 90 min.



[NaClO₂],0.2 m mole/l;Temperature,70 °C;
M/L ratio,1:50;Reaction Time,90 min.

Figure 5 Monomer concentration vs. % polymer yield. (●) %GY; (+) %H; (*) %TC; (□) %GE; [NaClO₂], 0.2 mmol/L; Temp. 70°C; M/L ratio 1 : 50; reaction time, 90 min.

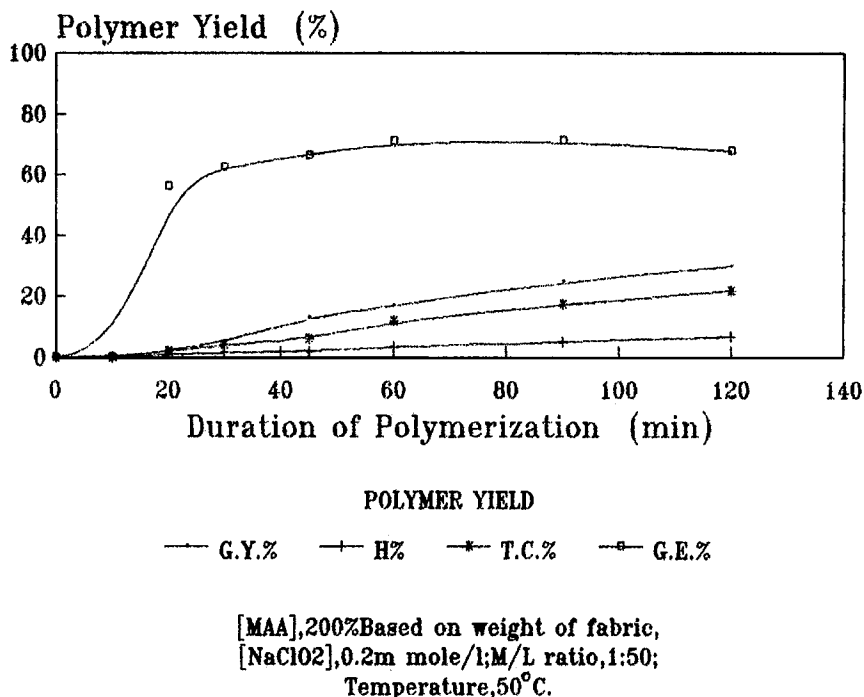


Figure 6 Duration and temperature vs. % polymer yield. (●) %GY; (+) %H; (*) %TC; (□) %GE; [MAA] 200% based on weight of fabric; [NaClO₂], 0.2 mmol/L; M/L ratio, 1 : 50; Temp. 50°C.

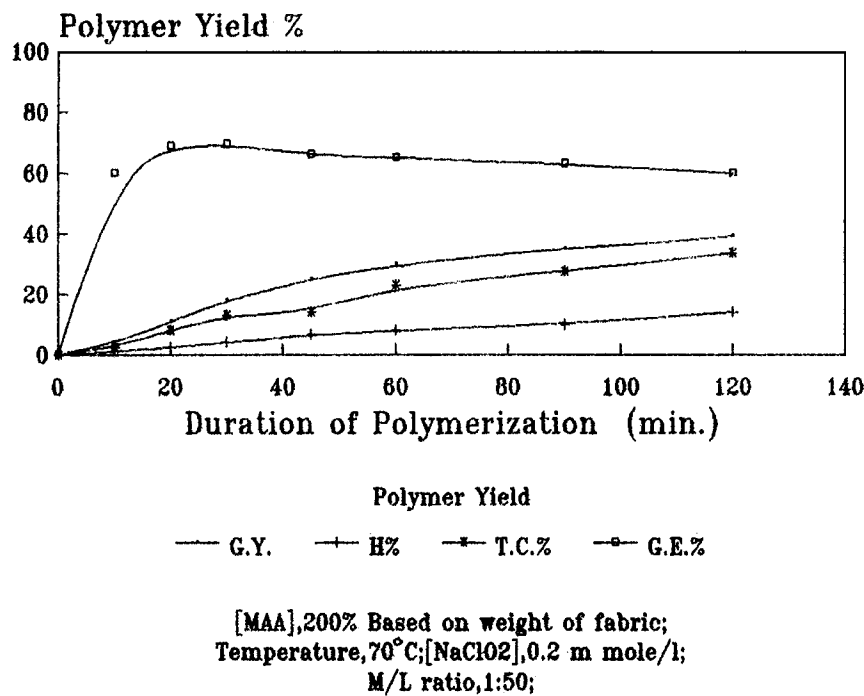


Figure 7 Duration and temperature vs. % polymer yield. (●), %GY; (+), %H; (*) %TC; (□) %GE; [MAA] 200% based on weight of fabric; [NaClO₂] 0.2 mmol/L; M/L ratio, 1 : 50; Temp., 70°C.

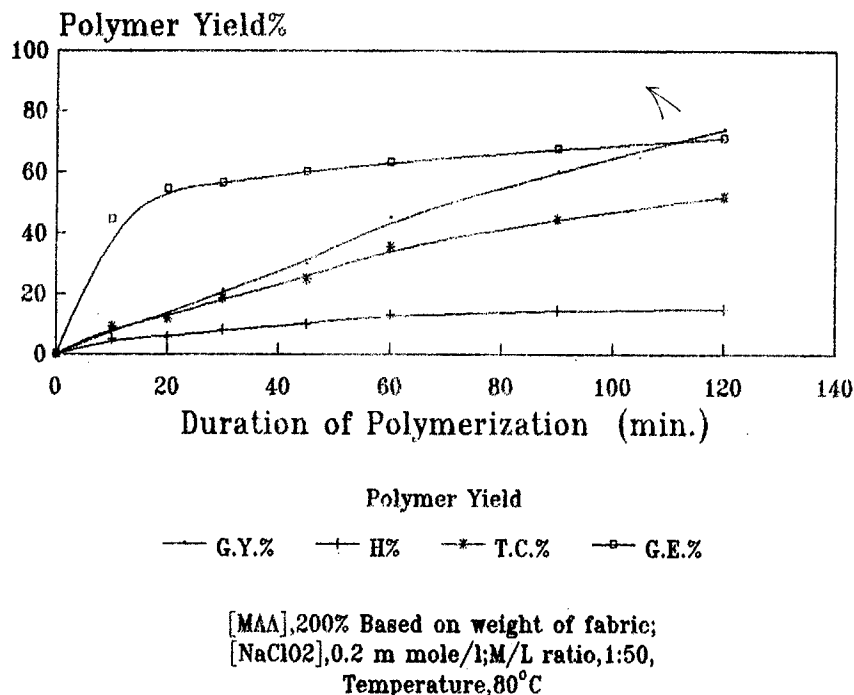


Figure 8 Duration and temperature vs. % polymer yield (●), %GY; (+) %H; (*) %TC; (□) %GE; [MAA] 200% based on weight of fabric; [NaClO₂] 0.2 mmol/L; M/L ratio, 1 : 50; Temp., 80°C.

yield increases sharply by increasing the concentration of MAA within the range studied. This would be associated with higher availability of monomer molecules in the proximity of cellulose macroradicals at higher monomer concentration. It is understandable that cellulose macroradicals are immobile, and for grafting to occur the monomer should be in the vicinity of the cellulose. Similar situation is encountered with homopolymer formation and total conversion. On the other hand the graft efficiency decreases considerably after a certain MAA concentration, a point that suggests that the homopolymer prevails over grafting at higher MAA concentration.

Polymerization Temperature

Figures 6–8 show the effect of polymerization temperature on the polymer yield. It is clear that the graft yield, homopolymer, and total conversion increase by raising the polymerization temperature from 50 to 80°C. The acceleration of the magnitude of polymerization upon raising the temperature could be associated with the favorable effect of temperature on: (a) decomposition of the redox system in question, giving rise to more free radicals, (b) swellability of viscose fabric and mobility of the monomer molecules, allowing better diffusion of

monomer from aqueous phase to fiber phase, and (c) rate of initiation and propagation of polymer chains. On the other hand, the graft efficiency is as high as 70% when polymerization reaction was carried out at 80°C for 2 h.

Figures 6–8 show also that at higher temperatures, the grafting reaction shows an initial fast rate followed by a slower one. Depletion in both monomer and initiator concentrations as polymerization reaction proceeds account for this.

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