

Potassium Permanganate/Thioureadioxide Redox System-Induced Grafting of Methacrylic Acid onto Loomstate Cotton Fabric

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SYNOPSIS

Graft polymerization of methacrylic acid (MAA) to loomstate cotton fabric using the KMnO_4 /thioureadioxide system as the initiator was studied under different polymerization conditions. The polymerization reaction was assessed with respect to 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 , thioureadioxide, and MAA as well as liquor ratio, reaction time, and temperature of polymerization. Based on a detailed investigation of these parameters, the optimal condition for grafting is KMnO_4 0.045 g/L, thioureadioxide 0.03 g/L, material to liquor ratio 1 : 30, MAA 100% (owf), temperature 80°C, and time 60 min. A reaction mechanism for the polymerization reaction is also reported. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Grafting of vinyl monomers on cellulose and modified cellulose has been the subject of several investigations.¹⁻¹⁰ The latter emphasizes the importance of such studies in elucidating the kinetics and mechanisms of the graft copolymerization reactions. They also provide the information that is required for improvements of the cellulose materials with a view to enlarge the range of utilization of these materials.

Recently, we developed conditions for vinyl graft copolymerization onto cellulose and modified cellulose in the fabric form¹¹⁻¹⁴ with little or no formation of a homopolymer. The system used was based on the utilization of starch-sized cotton fabric (loomstate fabric) or loomstate viscose fabric, using KMnO_4 in the presence of different activators for inducing graft polymerization of vinyl monomers on the fabric.

Considering the information gained from these recent studies, this work presents a detailed investigation of different factors affecting the grafting of

methacrylic acid onto loomstate cotton fabric using the KMnO_4 /thioureadioxide system.

EXPERIMENTAL

Materials

Loomstate cotton fabric (greige fabric), plain weave (36 picks, 56 ends/cm) was used as received from the mill. Methacrylic acid (MAA) was used without further purification. A nonionic wetting agent, namely, Nonidet LE, was kindly supplied by Shell Textile Chemicals, Cairo, Egypt. Potassium permanganate and thioureadioxide [$(\text{NH}_2)_2 - \text{C} = \text{SO}_2$] were reagent-grade chemicals.

Procedures

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

Treatment with KMnO_4

The loomstate cotton fabric (known weight) was impregnated in an aqueous solution containing a

specific concentration of KMnO_4 and 2 g/L of non-ionic wetting agent. The treatment was carried out at 40°C for 20 min using a material-to-liquor ratio of 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 cotton fabric (known weight) was introduced in a 100 mL stoppered conical flask containing an aqueous solution of MAA, thioureadioxide (TUD), and 2 g/L of a nonionic wetting agent. A material-to-liquor ratio of 1 : 30 was used and the reaction was carried out with continuous shaking. More details about the 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

Because of the loss in the original weight of the loomstat cotton fabric due to removal of the sizing agent by the KMnO_4 treatment, the percentage graft yield (% GY) was calculated as follows:

$$\% \text{GY} = \frac{w_2 - w_1}{w_1} \times 100$$

where w_2 = dry weight of the graft sample and w_1 = dry weight of loomstate cotton fabric after KMnO_4 treatment.

Percentages 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 the reported method^{13,15}:

$$\% \text{TC} = \frac{x_1 - x_2}{x_1} \times 100$$

$$\% \text{GE} = \frac{x_3}{x_1 - x_2} \times 100$$

$$\% \text{H} = \frac{x_1 - x_2 - x_3}{x_1} \times 100$$

where x_1 , x_2 , and x_3 are the weight of the blank

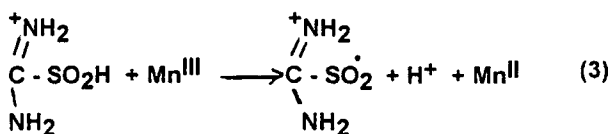
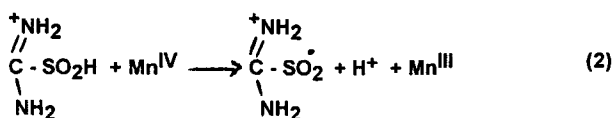
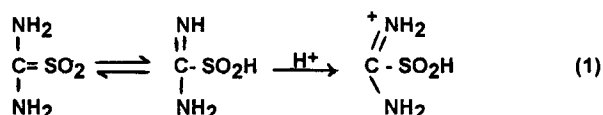
monomer, the weight of the residual monomer, and the weight of the grafted monomer, respectively.

RESULTS AND DISCUSSION

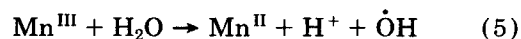
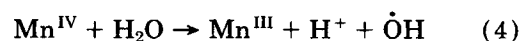
To study the grafting of MAA onto loomstate cotton fabric using the KMnO_4 /TUD system, the graft polymerization reaction was carried out under different conditions. Variables studied include the concentration of KMnO_4 , TUD, and MAA (monomer) as well as material-to-liquor ratio, duration, and temperature of polymerization. However, before going into a 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

Previous studies¹¹ have shown that a substantial amount of MnO_2 was deposited on the loomstate cotton fabric when the latter was soaked in KMnO_4 solution. In the presence of a reductant such as TUD and in an acidic medium, formation of primary radical species occurs as a result of the action of the TUD on the deposited MnO_2 . The isothioureadioxide radical ions constitute the primary radical species and are possibly formed as shown by the mechanism suggested by eqs. (1)–(10)¹⁶:



Other free-radical species, namely, the hydroxyl radical, may also be formed:

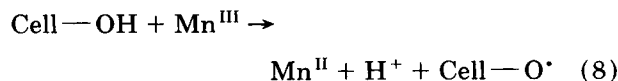
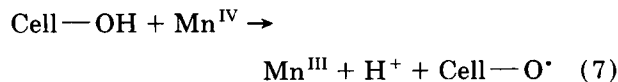


Once these free-radical species (R^{\cdot}) are created, they produced a cellulose macroradical via direct

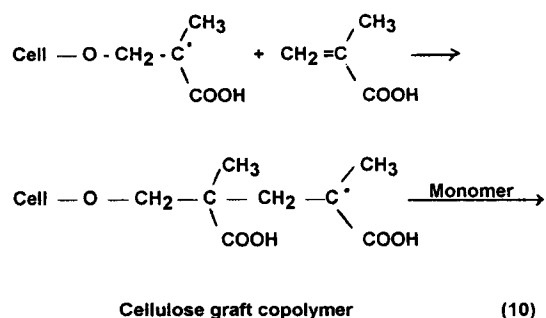
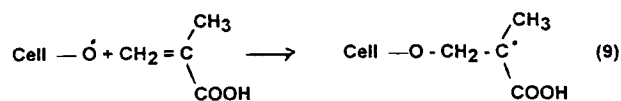
abstraction of the hydrogen atom from the hydroxyl groups of the cellulose molecules; thus:



Cellulose macroradicals may also be formed by direct attack of Mn^{IV} or Mn^{III} ions on the cellulose molecule via abstraction of the hydrogen atom¹⁷:



In the presence of a vinyl monomer (MAA), 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. Subsequent addition of monomer molecules to the initiated chain propagates grafting onto the cellulose:



Potassium Permanganate Concentration

Samples of loomstate cotton fabric were independently treated with a solution containing a different concentration of KMnO₄ (0.0–0.075 g/L) and wetting agent (2 g/L) at 40°C for 20 min using a material-to-liquor ratio of 1 : 30. The samples were then subjected to graft polymerization with MAA in the presence of 0.02 g/L TUD. The percentage polymer yield (graft yield, homopolymer, total conversion, and graft efficiency) was determined. The results obtained are shown in Figure 1. It is seen that the graft yield increases significantly by increasing the KMnO₄ up to 0.045 g/L. Above this concentration,

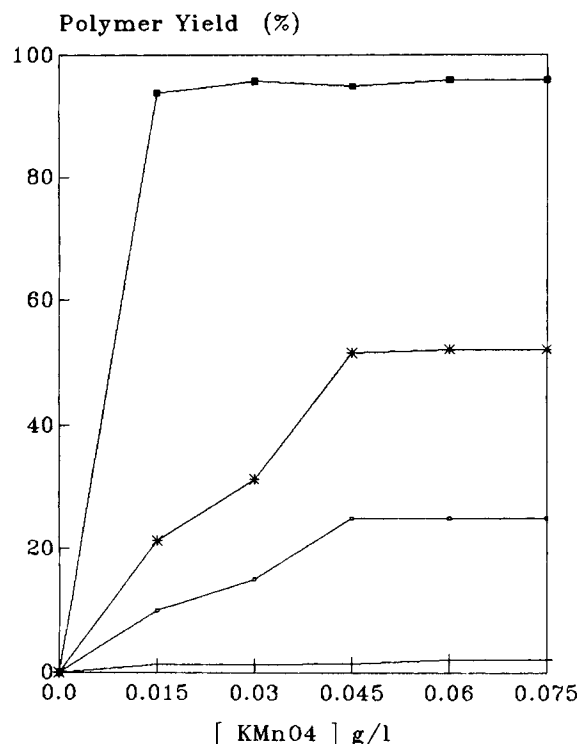
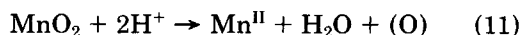


Figure 1 Potassium permanganate concentration vs. % polymer yield: (□) % GY; (+) % H; (*) % TC; (■) % GE; [MAA], 50% (owf); [TUD], 0.02 g/L; material-to-liquor ratio, 1 : 30; [wetting agent], 2 g/L; temperature, 80°C; time, 60 min.

the graft yield levels off. The same holds true for total conversion and grafting efficiency but the latter tends to levels off after a KMnO₄ concentration of 0.03 g/L. On the other hand, the magnitude of homopolymerization is rather very low irrespective of the initiator concentration, a point which signifies the potentiality of this method with respect to grafting of MAA onto cotton fabric. That grafting efficiency attains an average value of ca. 95% speaks of this.

The enhancement in grafting by increasing KMnO₄ concentration signifies the necessity of the presence of a certain amount of deposited MnO₂ on the cotton fabric to act, thereupon producing, ultimately, cellulose macroradicals capable of initiating grafting. On the other hand, the leveling off of grafting after certain KMnO₄ concentration could be associated with (a) a lower rate of monomer diffusion from the aqueous phase to the fiber phase by virtue of excess deposited MnO₂ colloidal particles, (b) a higher production of inhibiting oxygen at higher MnO₂ concentration due to the side reaction as shown by eq. (11), and (c) a faster rate of termination, par-

ticularly via bimolecular collision between two chain radicals because of the abundance of primary free-radical species:



Thioureadioxide Concentration

Figure 2 shows the effect of TUD concentration on the percentage polymer yield when the cellulose—MnO₂—TUD redox system was used to induce grafting of MAA onto cotton fabric. As is evident, the graft yield increases significantly by increasing the thioureadioxide concentration up to 0.03 g/L, then decreases. The same situation is encountered with total conversion and grafting efficiency. Meanwhile, the magnitude of the homopolymer increases by increasing the TUD concentration within the range studied.

The enhancement in percentage polymer yield by increasing TUD concentration up to 0.03 g/L is perhaps due to the generation of extra free-radical species as shown by eqs. (2) and (3). On the other hand, a decrement in percentage polymer yield upon using

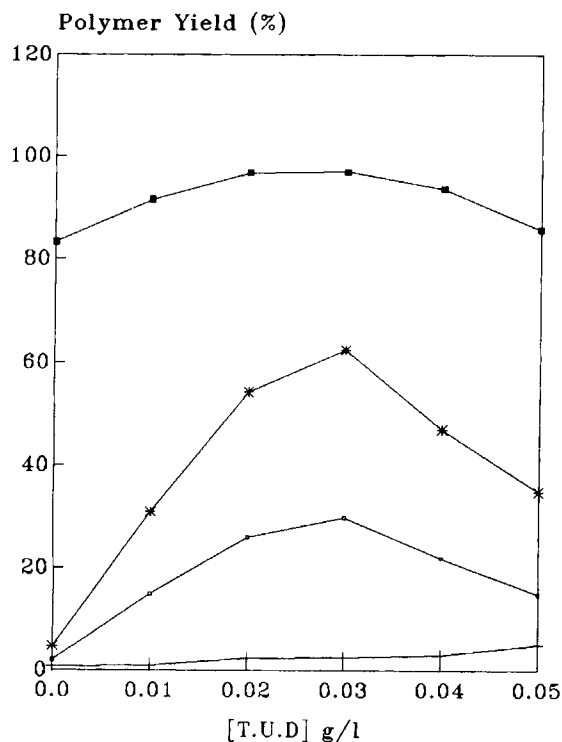


Figure 2 Thioureadioxide concentration vs. % polymer yield: (□) % GY; (+) % H; (*) % TC; (■) % GE; [KMnO₄], 0.045 g/L; [MAA], 50% (owf); [wetting agent], 2 g/L; material-to-liquor ratio, 1 : 30; temperature, 80°C; time, 60 min.

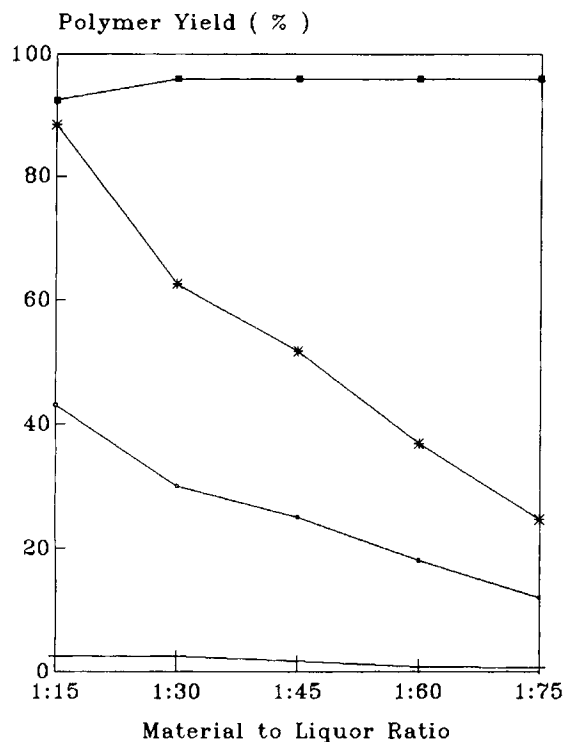


Figure 3 Liquor ratio vs. % polymer yield: (□) % GY; (+) % H; (*) % TC; (■) % GE; [KMnO₄], 0.045 g/L; [TUD], 0.03 g/L; [MAA], 50% (owf); [wetting agent], 2 g/L; temperature, 80°C; time, 60 min.

a higher concentration of TUD (above 0.03 g/L) suggests that some species must have been generated and are acting efficient radical scavengers (i.e., adverse effect of TUD).

It is as well to note that the magnitude of the homopolymer, though poor, tends to have a value of 5% only at TUD concentration of 0.05 g/L, which is the highest concentration used in this study (Fig. 2). A concentration lower than this brings about values that never exceed 3%. This again calls for the potentiality of this method of initiation. Grafting efficiency of 95% could be easily achieved.

Liquor Ratio

Figure 3 shows the effect of liquor ratio on the said polymerization criteria, namely, graft yield, homopolymer, total conversion, and grafting efficiency. It is seen that the graft yield, homopolymer, and total conversion decrease as the liquor ratio increases within the range studied. This suggests that (a) the availability of the monomer in the vicinity of the cellulose is lower at larger than at smaller liquor ratios and (b) the rate of diffusion of the monomer from the liquor phase to the fiber phase is dependent

on the volume of the liquor ratio. Transfer of the monomer from the large liquor to the cellulose proceeds in a low rate, perhaps due to the smaller surface area of cellulose compared to the liquor. On the other hand, grafting efficiency is characterized by an apparent increment up to a liquor ratio of 30, then levels off, a point which, rather, reflects the dependence of grafting efficiency on the amount of the graft in relation to its own amount plus the amount of the homopolymer.

Duration of Polymerization Reaction

Figures 4–6 show the percentage polymer yield (expressed as graft yield, homopolymer, total conversion, and graft efficiency) for the polymerization of MAA as a function of reaction time using a cellulose–MnO₂–TUD redox system at 60, 80, and 90°C. It is seen that for a given temperature the graft yield, total conversion, and homopolymer increase by increasing the reaction time within the range studied. It is certain, however, that at the final stage (90 min) the magnitude of the graft yield follows the order 80 > 90 > 60°C. A different situation is encountered for graft efficiency; the latter is charac-

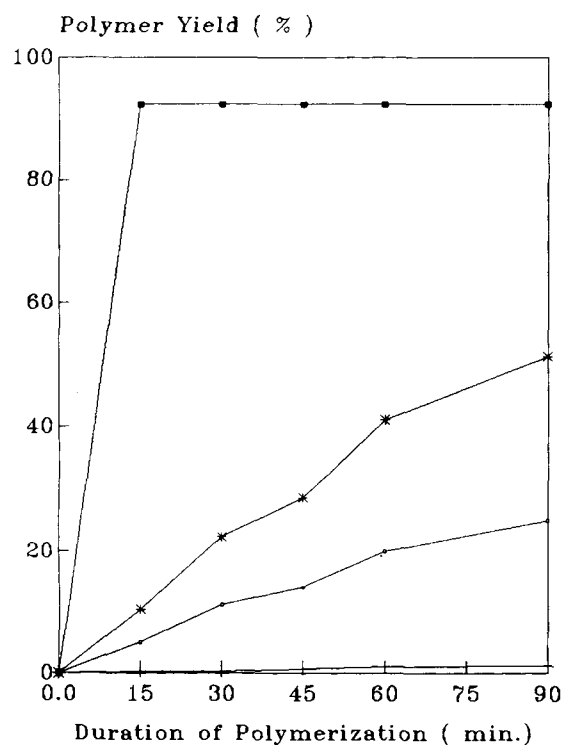


Figure 4 Duration and temperature vs. % polymer yield: (□) % GY; (+) % H; (*) % TC; (■) % GE; [KMnO₄], 0.045 g/L; [TUD], 0.03 g/L; [MAA], 50% (owf); [wetting agent], 2 g/L; material-to-liquor ratio, 1 : 30; temperature, 60°C.

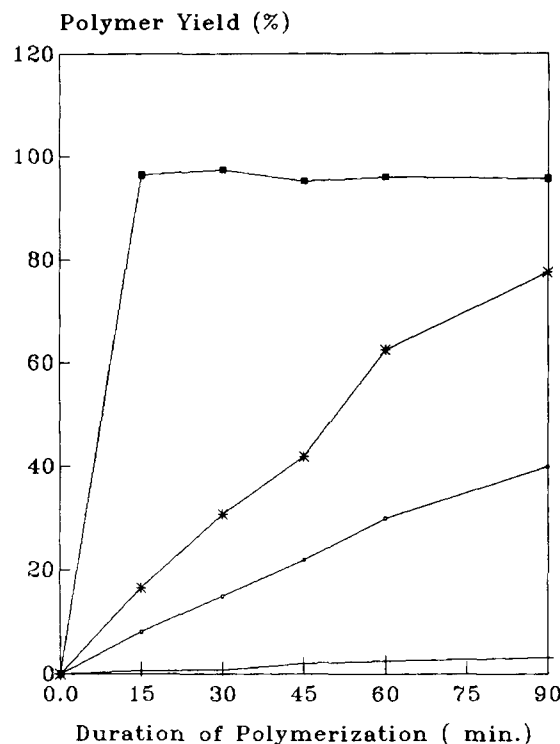


Figure 5 Duration and temperature vs. % polymer yield: (□) % GY; (+) % H; (*) % TC; (■) % GE; [KMnO₄], 0.045 g/L; [TUD], 0.03 g/L; [MAA], 50% (owf); [wetting agent], 2 g/L; material-to-liquor ratio, 1 : 30; temperature, 80°C.

terized by an initial fast rate, then levels off. Depletion in both the monomer and initiator concentration as the polymerization reaction proceeds and/or a faster rate of termination of the growing grafted polymer chains^{18,19} would account for this.

Polymerization Temperature

To investigate the effect of temperature on the rates of polymerization (expressed as graft yield, homopolymer, total conversion, and graft efficiency), loomstate cotton fabric samples were subjected to graft polymerization with MAA (50% owf) using a cellulose–MnO₂–TUD redox system at different temperatures, viz., 60, 80, and 90°C, for varying lengths of time (15–90 min). Figures 4–6 show the rates of polymerization. It is clear that the rates of grafting, homopolymerization, and total conversion increase by raising the polymerization temperature from 60 to 90°C.

The acceleration of the rates of polymerization upon increasing the temperature from 60 to 80 or 90°C could be associated with the favorable effect of temperature on the (a) reaction of TUD with MnO₂, thus increasing the free-radical species in the

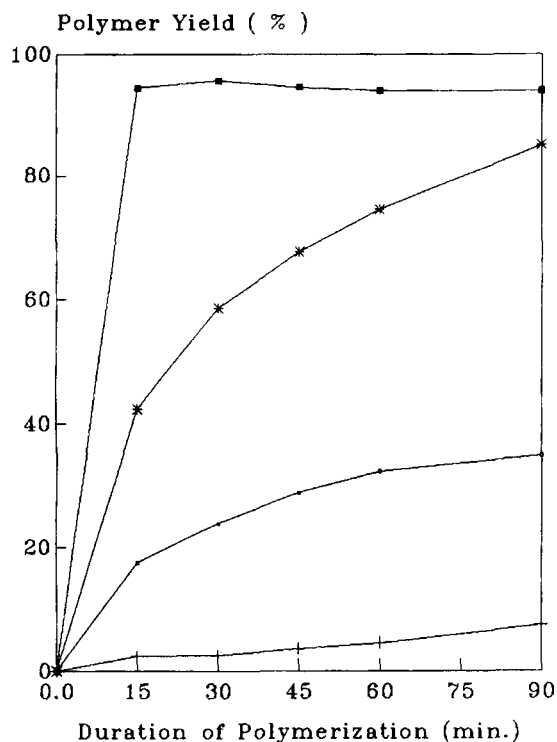


Figure 6 Duration and temperature vs. % polymer yield: (□) % GY; (+) % H; (*) % TC; (■) % GE; $[\text{KMnO}_4]$, 0.045 g/L; [TUD], 0.03 g/L; [MAA], 50% (owf); [wetting agent], 2 g/L; material-to-liquor ratio, 1 : 30; temperature, 90°C.

reaction medium, (b) reaction of the free-radical species, i.e., the hydroxyl and isothioureadioxide radicals, with cellulose to bring about cellulose macroradicals, (c) the swellability of the cotton fabric and mobility of the monomer molecules, allowing better diffusion of monomer from the aqueous phase to the fiber phase, and (d) rate of initiation and propagation of the polymer chains. On the other hand, the higher rate of homopolymerization observed upon increasing the temperature up to 90°C could be ascribed to the dissolution of the amount of homopolymer formed during the initial stages in the reaction medium, which seems to create a viscous environment, leading to the gel effect.²⁰ The latter impedes termination of the growing chains, thereby giving rise to a homopolymer with higher molecular weight.

Monomer Concentration

Figure 7 shows the effect of MAA concentration on the percentage of polymer yield. The MAA concentration used ranges from 10 to 100%, based on the weight of the fabric (owf). It is seen that the graft yield and the homopolymer increase by increasing

the monomer concentration within the range studied. On the other hand, the total conversion and grafting efficiency increase significantly by increasing the monomer concentration up to 50% (owf), then decrease as the concentration of monomer increases.

The enhancement in grafting and/or homopolymer by increasing monomer concentration (within the range studied) would be associated with the higher availability of monomer molecules in the proximity of cellulose macroradicals as well as in the polymerization medium 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. It is also understandable that greater availability of the monomer in the polymerization medium acts in favor of molecular collision, thereby enhancing polymerization, in general, or homopolymer formation, in particular. On the other hand, the decrease of total conversion and grafting efficiency observed after a concentration of MAA of 50% (owf) suggests that much of Mn^{IV} and TUD seems to be consumed during the conversion of a certain amount of the monomer to polymer.

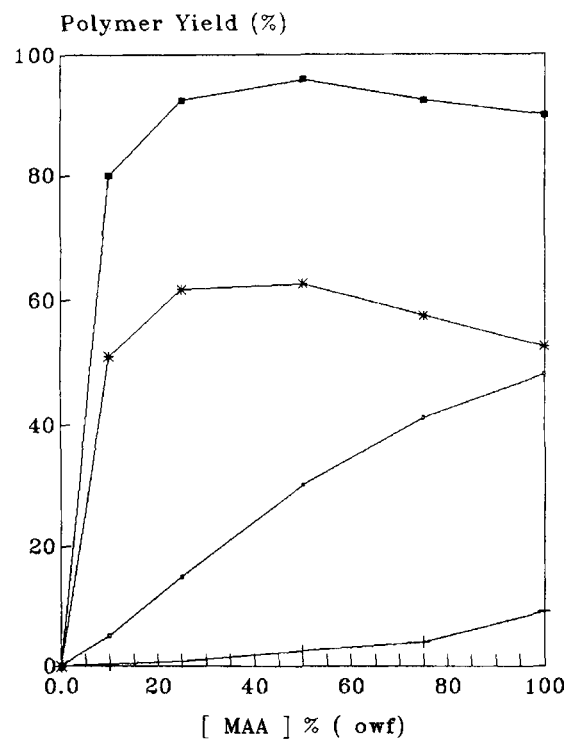


Figure 7 Monomer concentration vs. % polymer yield: (□) % GY; (+) % H; (*) % TC; (■) % GE; $[\text{KMnO}_4]$, 0.045 g/L; [TUD], 0.03 g/L; [wetting agent], 2 g/L; material-to-liquor ratio, 1 : 30; temperature, 80°C; time, 60 min.

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