

# Improved Synthesis of Poly(MAA)–Starch Graft Copolymers

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**ABSTRACT:** Graft copolymerization of methacrylic acid (MAA) onto starch using a potassium persulfate/sodium thiosulfate redox initiation system was investigated. Emphasis was placed on the promotion of graft formation while minimizing homopolymerization. This could be achieved through a thorough investigation into the major factors affecting the polymerization reaction such as the state of the starch, redox ratio of the initiator, monomer and initiator concentrations, time and temperature of polymerization, and material-to-liquor ratio. The results obtained imply that the magnitude of the polymer yield including total conversion, graft yield, and homopolymer are determined by these factors. The yield is favored under the influence of higher temperature, longer time, short liquor, and increased monomer and initiator concentrations. A poly(MAA)–starch graft copolymer is the main product of the polymerization reactions only when starch was preswelled (through cooking prior to grafting). Moreover, this grafted product could be precipitated by more dilution with water and easily separated by filtration. Hence, the results of the current work formed the basis of a novel method for the synthesis of poly(MAA)–starch graft copolymers. The mechanisms involved in the synthesis are reported. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1709–1715, 1998

**Key words:** starch; sizing agent; size recovery; polymer; polymerization; redox initiation; ion exchanger

## INTRODUCTION

Graft copolymerization of starch with acrylic monomers presents a powerful potential way for imparting to starch new and desirable properties. It was and still is the subject of numerous publications. Methods based on different initiation systems have been reported for the graft polymerization of acrylic and methacrylic acid.<sup>1,2</sup> Benzoyl peroxide,<sup>3</sup> potassium persulfate,<sup>1–3</sup> ceric ion,<sup>4–6</sup> redox systems,<sup>7–10</sup>  $\gamma$ -ray and electron beam irradiation, and photolysis<sup>2,11</sup> have been used as initiators or initiating systems. These systems, however, are of low efficiency in graft polymerization,

and, as a rule, grafting is accompanied by the formation of substantial amounts of homopolymers.

The scientific and practical significance of synthesizing graft copolymers of starch without homopolymer formation has been emphasized. As a matter of fact, effective methods of synthesizing other graft copolymers have been developed.<sup>12,13</sup>

Previous reports<sup>1</sup> have disclosed that graft polymerization of acrylic acid onto starch using potassium persulfate as an initiator is accompanied by a huge amount of homopolymer formation and, indeed, the homopolymer prevails largely over grafting. The same holds true for the potassium persulfate/sodium thiosulfate redox system.<sup>13</sup>

The present work was undertaken with a view to develop a novel method for grafting with the least amount of homopolymer formation. Grafting

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of starch was carried out using methacrylic acid as the vinyl monomer and  $K_2S_2O_8/Na_2S_2O_3$  as the redox initiation system. Utilization of highly swollen (cooked) starch and the precipitation of the starch graft copolymers by mere dilution with water constitute the salient features and novelty of the devised method in question.

## EXPERIMENTAL

### Materials

Maize starch was kindly supplied by the Egyptian Starch and Glucose Manufacturing Co., Cairo. Methacrylic acid (MAA, Merck, Germany) was freshly distilled,  $d_0^{20} = 1.0157$ . Potassium persulfate ( $K_2S_2O_8$ ) and sodium thiosulfate ( $Na_2S_2O_3 \cdot 5H_2O$ ), potassium bromide (KBr), and potassium iodide (KI) were of laboratory-grade chemicals.

### Preparation of Highly Swollen Starch

Starch was cooked at 95°C in an oil bath for 30 min under mechanical stirring (400 rpm). After cooking, the temperature was lowered to 25°C and the mechanical stirring was continued but at the minimum power.<sup>14</sup> The cooked starch will be referred to as highly swollen starch (HSS).

### Polymerization Procedure

The graft-copolymerization reaction was carried out in a 250-mL three-neck round flask equipped with a mechanical stirrer. Starch was added to the reaction flask as a slurry in the case of native starch, whereas it was added as a HSS in the case of cooked starch. The starch/liquor ratio was adjusted with distilled water to attain a ratio of 1 : 20. MAA was then introduced into the reaction flask. The latter was heated in a water bath until the desired temperature was reached. After stirring well, the initiator components, that is, potassium persulfate and sodium thiosulfate, were added within 1 min. The polymerization reaction was carried out under normal atmospheric conditions. The flask contents were kept under continuous stirring (300 rpm) and the reaction temperature at 70°C for the polymerization to proceed. After the desired reaction time, the flask contents were poured over 1 L cold water, where a precipitate was formed. This precipitate consisted of the poly(MAA)–starch graft copolymer and the homo-

polymer, that is, poly(MAA). The precipitate was filtered and washed several times merely with cold water to remove the unreacted MAA. The precipitate was dried at ambient conditions. The homopolymer was separated from the graft copolymer by Soxhlet extraction. Methanol was used for the extraction. The extracted solution was concentrated by vacuum distillation, and a portion of about 50 mL of the concentrated solution was evaporated until dry and the residue was weighed. On the other hand, the graft copolymer, after being subjected to extraction, was dried in an electric oven at 70°C for 2 h. The graft yield was estimated gravimetrically and chemically by the determination of the carboxyl content.

### Analysis

#### Carboxyl Content

The carboxyl content was measured according to a reported method.<sup>15</sup>

#### Total Conversion Percent (TC%)

The TC% was calculated via quantitative estimation of the free double bonds of MAA before, during, and after the polymerization process according to a reported method.<sup>16,17</sup>

#### Graft Yield Percent (GY%)

The amount of the obtained graft copolymer was determined from the increase of the starch mass after the extraction of the homopolymer and drying:

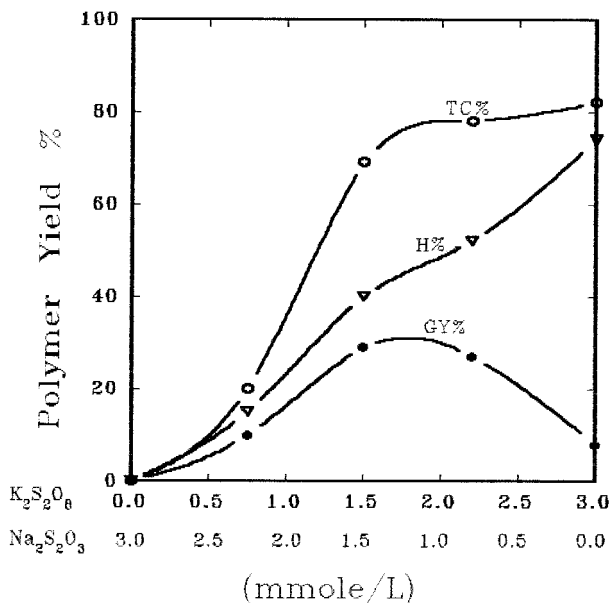
$$GY\% = \frac{W_1 - W_0}{W_0} \times 100$$

$$\text{Homopolymer percent (H\%)} = \frac{W_2 - W_1}{M} \times 100$$

where  $W_0$  is the initial weight of the dry starch;  $W_1$ , the weight of the extracted product;  $W_2$ , the weight of the polymerization crude product; and  $M$ , the weight of the monomer used.

#### Viscosity

The viscosity of the crude polymerization product (in the sodium form) was measured using a coaxial rotatory viscometer (Haake-RV 20) at 80°C and a shear rate of 516  $s^{-1}$ .



**Figure 1** Effect of persulfate/thiosulfate ratio on polymer yield: (○) *TC*%; (●) *GY*%; (▽) homopolymer [persulfate/thiosulfate], 3 mmol/L; [MAA], 6%; temperature, 70°C; time, 2 h; material/liquor ratio 1 : 20.

### Concentration

The concentration was measured using a hand refractometer (Kruess-HRT-32) at 25°C.

## RESULTS AND DISCUSSION

Graft copolymerization of MAA with starch was carried out using a  $K_2S_2O_8/Na_2S_2O_3$  redox initiation system. Highly swollen starch was used under a variety of polymerization conditions with a view to minimize homopolymer formation. Results of these studies along with their appropriate discussion are given below.

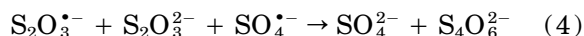
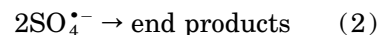
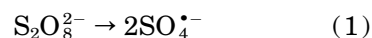
### Effect of Initiator

Figure 1 shows the effect of the persulfate/thiosulfate ratio on the polymer yield. The latter refers to total conversion (*TC*), homopolymer (*H*), and graft yield (*GY*). Aqueous polymerization of MAA was induced by the persulfate/thiosulfate redox system in the presence of HSS.

It is seen (Fig. 1) that at a persulfate/thiosulfate ratio of 0/3 mmol/L no polymerization occurs since the polymer yield is zero. The opposite situation is encountered when persulfate/thiosulfate at a ratio 3/0 mmol/L was used; significant poly-

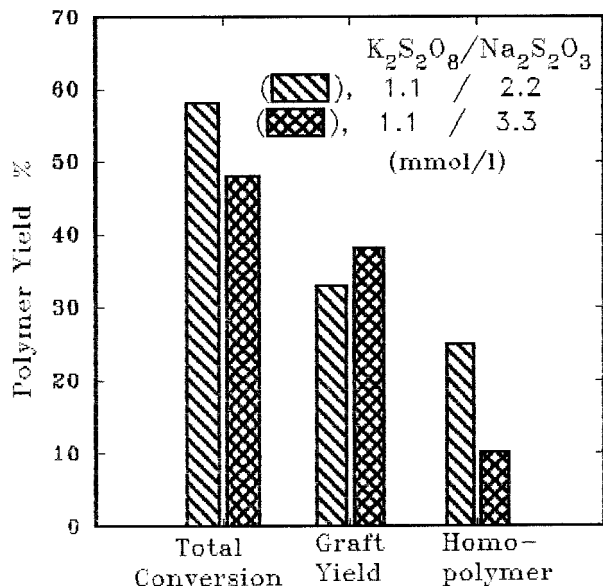
merization takes place as is evident by the high values of the *TC*, *H*, and *GY*. Persulfate/thiosulfate ratios between these two extremes bring about polymer yield values which determine the trend for *TC*, *H*, and *GY*, while the *H*% increases significantly by increasing the persulfate in the redox ratio. The *TC*% follows a similar trend but tends to approach leveling off at a persulfate/thiosulfate ratio of 2.5/0.5 mmol/L. On the other hand, the *GY*% exhibits a maximum at a persulfate/thiosulfate ratio in the range 1.5–2.0/1.5–1.0 mmol/L.

The above results signify two major features: First, the persulfate decomposition gives rise to free radicals capable of initiating the polymerization of MAA which occurs in the absence and presence of the thiosulfate. Second, the presence of the thiosulfate along with the persulfate is a must for achieving a higher graft yield. The thiosulfate seems to help establish a continuous process for free-radical creation as suggested by the following reaction scheme<sup>18–21</sup>:



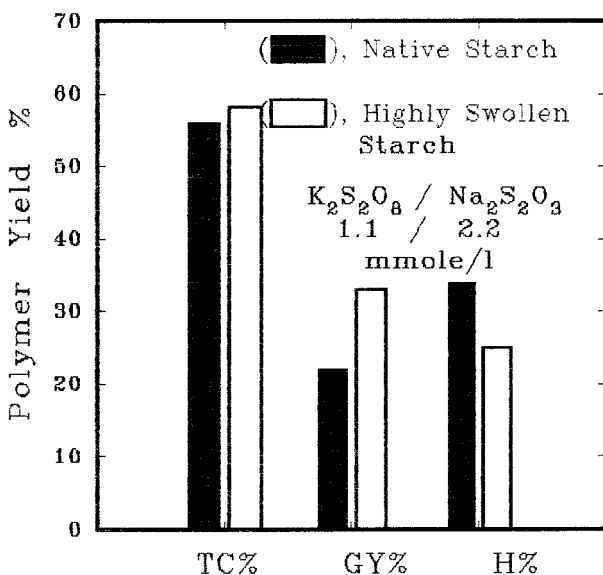
Obviously, in the presence of thiosulfate, the initiation of free radicals appears to be a continuous process according to reactions (3), (5), and (6), whereas reactions (2) and (4) act in favor of free-radical disappearance. It is believed that in the presence of thiosulfate there are different free radicals, the sulfate, the thiosulfate, and the hydroxyl radicals, which can attack the starch, resulting in hydrogen abstraction and the formation of free radicals on the starch molecules. The starch radicals so formed induce the grafting of MAA onto the starch. Concurrently with grafting, the homopolymerization of MAA occurs under the initiating action of the free radicals.

The higher values of *TC*% and *H*% observed even in absence of thiosulfate calls for the contribution of the starch and the monomer as reducing components which assist the decomposition of the persulfate.<sup>22</sup> Besides, the homopolymerization of MAA seems to occur and proceed much faster than does grafting.<sup>23</sup>

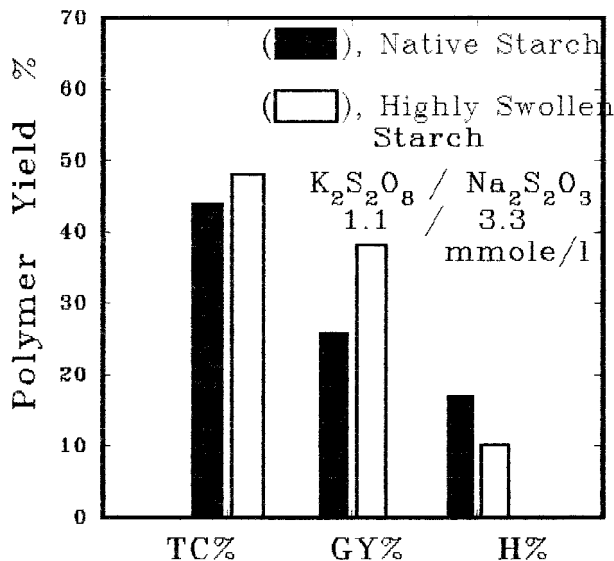


**Figure 2** Dependence of total conversion, graft yield, and homopolymer on the persulfate/thiosulfate ratio. Substrate: HSS; [MAA], 6%; temperature, 70°C; time, 3 h; material/liquor ratio, 1 : 20.

Trials were done to accentuate the magnitude of grafting. Figure 2 discloses that this could be achieved by using the redox initiator at persulfate/thiosulfate ratios of 1.1/2.2 and 1.1/3.3 mmol/L, but with the certainty that the latter



**Figure 3** Comparison between native starch and highly swollen starch on the polymer yield ( $TC\%$ ,  $GY\%$ , and  $H\%$ ): [persulfate/thiosulfate], 1.1/2.2 mmol/L; [MAA], 6%; temperature, 70°C; time, 3 h; material/liquor ratio, 1 : 20.



**Figure 4** Comparison between native starch and HSS on the polymer yield ( $TC\%$ ,  $GY\%$ , and  $H\%$ ): [persulfate/thiosulfate], 1.1/3.3 mmol/L; [MAA], 6%; temperature, 70°C; time, 3 h; material/liquor ratio, 1 : 20.

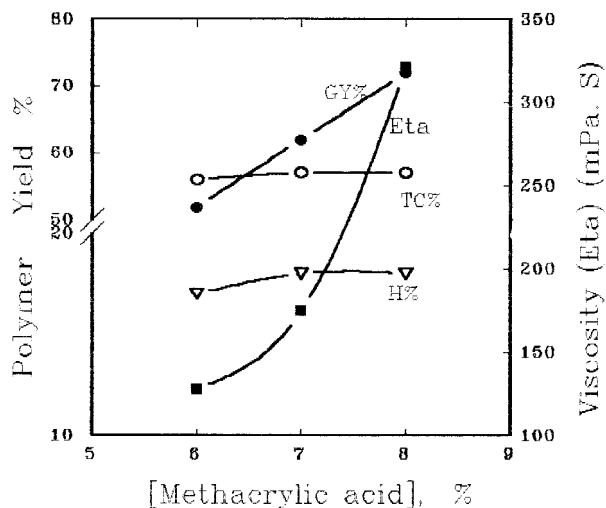
ratio is better than the former. This is, indeed, substantiated by the results shown in Figures 3 and 4 where the two ratios were independently employed to induce the polymerization of MAA in the presence of native (unswollen) starch and highly swollen (cooked) starch.

Figures 3 and 4 reveal clearly that the magnitude of polymerization is favored in the presence of the HSS as compared with unswollen starch as evidenced by  $TC\%$ . They further reveal that grafting prevails over homopolymerization when HSS is used as evidenced vis-à-vis  $H\%$ . Beside providing a larger surface area, the HSS seems to be a better candidate for grafting by making the starch hydroxyls more accessible and available for the initiation and propagation of the graft.

#### Effect of Monomer Concentration

Figure 5 shows the effect of MAA concentration on the polymer yield and related viscosity. It is seen that the increasing of the MAA concentration is accompanied by a marginal increment in the percent total conversion and the homopolymer. Meanwhile, the graft yield increases significantly and so does the viscosity.

The significant enhancement in the  $GY\%$  by increasing the MAA concentration could be interpreted in terms of the greater availability of monomer molecules in the proximity of the starch



**Figure 5** Effect of MAA concentration on the polymer yield: (○) TC%; (●) GY%; (▽) H%; (■) viscosity. Polymerization conditions: substrate—HSS 10%; persulfate/thiosulfate, 1.1/3.3 mmol/L; temperature, 70°C; time, 2 h; material/liquor ratio, 1 : 20. Viscosity conditions: [solution], 10%; temperature, 80°C; rate of shear, 516 s<sup>-1</sup>.

at higher MAA concentration. It is understandable that the active centers on starch molecules are relatively immobile. Reaction of these macroradicals with the monomer would, therefore, essentially depend on the availability of the monomer in their vicinity.<sup>1</sup>

Based on the above, it is concluded that the swollen starch-MAA-persulfate/thiosulfate-water form a very promising system for the synthesis of the poly(MAA)-starch graft copolymer. The copolymerization reaction proceeds with little homopolymer formation, in accordance with previous reports.<sup>24,25</sup>

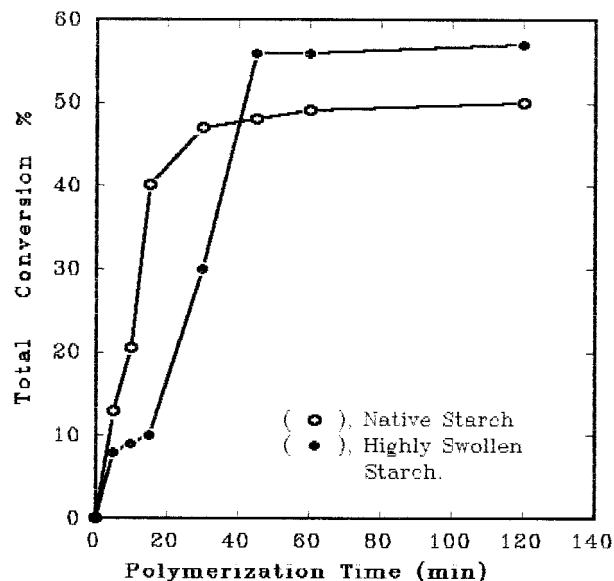
A salient feature of current work is the finding that the (MAA)-starch graft copolymer is the main product. Moreover, it could be precipitated by mere dilution with water. The precipitate is separated easily by filtration.

The effect of structural changes in the starch brought about by the polymerization of MAA at different concentrations in the presence of swollen starch on the apparent viscosity of the latter may be realized from Figure 5. The apparent viscosity was measured using a 10% solution of the polymerization products directly after ending the polymerization reaction. It is seen that the apparent viscosity increases significantly by increasing the MAA concentration, like the trend observed with the graft yield. This implies that the enhancement

in apparent viscosity is unequivocally due to the MAA grafts which are created and chemically built-in in the starch structure. As a result, the molecular size of the starch product under investigation increases—consequently, the apparent viscosity. This is rather in confirmation with the finding that the poly(MAA)-starch graft copolymer is the main product when MAA is polymerized with swollen starch under the condition used.

### Effect of Polymerization Time

Figure 6 shows the effect of polymerization time on the total conversion of MAA in the presence of native starch and HSS. The polymerization reaction was carried out at 70°C in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> at a ratio of 1.1/3.3 mmol/L. A starch-to-liquor ratio of 1 : 20 was employed using MAA at a concentration of 6%. It is seen (Fig. 6) that the polymerization reaction is characterized by an initial fast rate, followed by a much slower rate during the later stage of the reaction. This is observed with native starch as well as with HSS. However, the two substrates exhibit differences when the rates and magnitude of the total conversion are considered. Polymerization proceeds much faster during the initial stage of the polymerization reaction in the case of native starch



**Figure 6** Effect of duration of polymerization on total conversion when MAA was polymerized in the presence of native starch and HSS using the potassium persulfate/sodium thiosulfate (1.1/3.3 mmol/L) redox system. [MAA], 6%; temperature, 70°C; material/liquor ratio, 1 : 20.

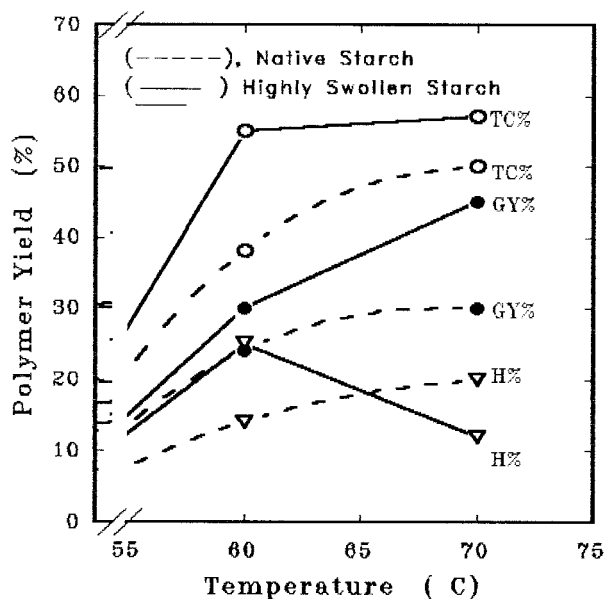
as compared with the HSS. The total conversion obtained with native starch during the later stage of polymerization continues to increase by increasing the time within the range studied, whereas it tends to level off in the case of the HSS. It is certain, however, that the maximum total conversion obtained after the longest time allowed (120 min) is higher with the highly swollen than with the native starch.

Differences in the rate of the polymerization and magnitude of total conversion observed with the two starch substrates under investigation reflects differences between the native starch and the HSS with respect to the (1) crystalline/amorphous ratio, (2) available surface area, (3) accessibility of the starch hydroxyls, (4) ease of undergoing modification and the onset of this on further reactions, and (5) ease of diffusion and adsorption of polymerization ingredients and their contribution in initiation, propagation, and termination of polymerization.

Current data suggest that native starch (by virtue of its supermolecular structure which plays a key role in the provision of grafting sites on the starch molecule) undergoes structural changes under the influence of the relatively initial higher amount of grafting. In combination with this is the depletion in the monomer and initiator concentration as well as the shortage in grafting sites on the starch molecule as the polymerization reaction proceeds. With the HSS, on the other hand, the limitation imposed by the fine physical structure is overcome since the HSS tends to acquire a 100% amorphous structure. This characteristic seems to offer a starch substrate with a more uniform structure which acts in favor of the regulation of the graft add-on, thereby the adverse effect caused by the higher initial amount of graft formation and its consequences on the structure of starch. In the meantime, factors (2)–(5) mentioned above help to establish a better condition for gradual and regular grafting during the initial stages of polymerization with subsequent higher grafting during the later stages of polymerization. Besides, the contribution of grafting in the total conversion is higher with the swollen starch than with native starch as already indicated.

### Effect of Temperature

Figure 7 shows the effect of temperature on the polymerization of MAA in the presence of the native starch and the swollen starch. The polymerization reaction was carried out using 10 g of the



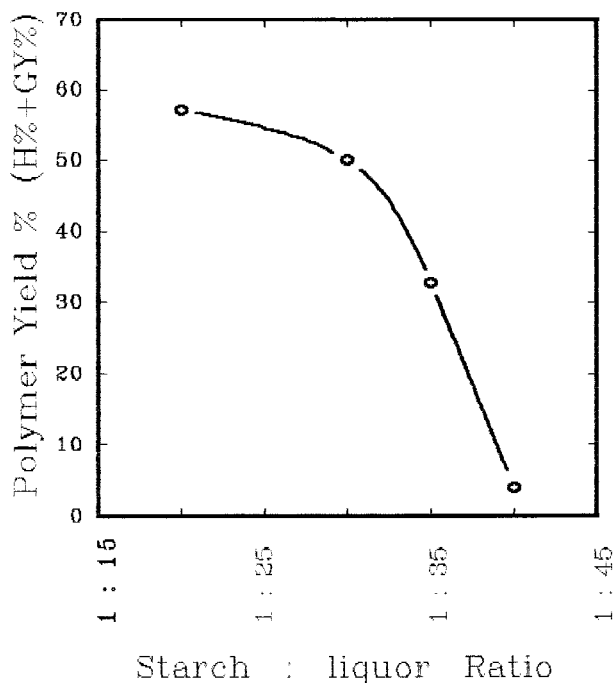
**Figure 7** Variation of the polymer yield percent with polymerization temperature: (-----) native starch; (—) HSS; (○) TC%; (●) GY%; (▽) H%; [persulfate/thiosulfate], 1.1/3.3 mmol/L; [MAA], 6%; time, 2 h; material/liquor ratio, 1 : 20.

starch substrate and  $K_2S_2O_8/Na_2S_2O_3$  (1.1/3.3 mmol/L), MAA (6%), and a material-to-liquor ratio of 1 : 20 for 2 h.

It is seen that the TC and GY are higher the higher the temperature. This is observed with the native starch and the swollen starch. However, the magnitudes of TC and GY obtained with the swollen starch are much higher than those for the native starch. On the other hand, the amounts of the homopolymer (H%) are equal in the presence of both substrates up to 60°C. At 70°C, on the other hand, the amount of the homopolymer is much lower in the presence of the swollen starch. The implication of this is that grafting prevails over homopolymerization at 70°C. Hence, utilization of swollen starch is advantageous in promoting grafting and this advantage is more significant when the polymerization is carried out at a temperature as high as 70°C.

### Starch/Liquor Ratio

Figure 8 shows the dependence of polymer yield on the starch/liquor ratio. Fixed weights of the swollen starch (10 g), MAA (6 g), and potassium persulfate/sodium thiosulfate (0.062/0.166 g) were used along with different amounts of water. The reaction was carried out at 70°C for 60 min.



**Figure 8** Dependence of the polymer yield on the material/liquor ratio. Substrate: HSS; [persulfate/thiosulfate], 1.1/3.3 mmol/L; [MAA], 6%; temperature, 70°C; time, 2 h.

The starch/water ratios examined ranged from 1 : 20 to 1 : 40.

It is observed that the polymer yield is higher the lower the starch/water ratio. As the latter increases, the polymer yield decreases. This could be interpreted in terms of molecular collision as the latter is favored at lower liquor ratios.<sup>1,10,26</sup>

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