

# Graft Copolymerization of Hydroxyethyl Methacrylate onto Chitosan

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**ABSTRACT:** Chitosan is a polysaccharide derived from chitin, which is commonly found in shellfish waste materials. The present work is concerned with the graft copolymerization of 2-hydroxyethylmethacrylate (HEMA) onto chitosan using thiocarbonation–potassium bromate for redox initiation. The combined effects of the principal reaction variables for the grafting reaction were studied systematically. This grafting reaction was studied with respect to percentages of graft yield (%G.Y.), homopolymer (%H.P.), and total conversion (%T.C.). A tentative polymerization mechanism is proposed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 683–702, 2001

**Key words:** chitosan; hydroxyethylmethacrylate; thiocarbonation–potassium bromate initiation; graft copolymerization

## INTRODUCTION

Chitin is derived from the shellfish waste of crab or shrimp, and has a structure similar to that of cellulose. It is also known to be biocompatible, biodegradable, and nontoxic, and thus has been used in drug-delivery systems and also in biomedical applications. However, because of its crystalline nature, chitin is difficult to dissolve. Chitosan, a deacetylated product of chitin, is easily dissolved in dilute organic acids such as acetic or formic acid, and has been utilized as films,<sup>1</sup> membranes,<sup>2–5</sup> and fibers,<sup>6</sup> and has been more widely used than chitin.<sup>7,8</sup>

The chemical modification of natural polymers is a promising method for the preparation of new materials. This enables one to introduce special properties and enlarge the field of potential applications of these abundant biopolymers. Among

the diverse modifications that are possible to achieve, grafting of synthetic polymers is a convenient method.<sup>9–12</sup> The properties of the resulting graft copolymers may be widely controlled by the characteristics of the side chains, including molecular structure, length, and number.

Graft copolymerization of chitosan with acrylonitrile; methylmethacrylate (MMA), using azobisisobutyronitrile (AIBN)<sup>13,14</sup>; MMA, using Fenton's reagent as redox initiator<sup>15</sup>; 2-hydroxyethylmethacrylate (HEMA) and acrylamide, using ceric (IV) salt as redox initiator<sup>16,17</sup>; and styrene, vinyl acetate, and acrylamide, using the  $\gamma$ -irradiation method have been reported in the literature.<sup>18,19</sup>

The present work is concerned with the graft copolymerization of 2-hydroxyethylmethacrylate (HEMA) onto chitosan using thiocarbonation–potassium bromate for redox initiation. The combined effect of the principal reaction variables for the grafting reaction were studied systematically. This grafting reaction was studied with respect to percentages of graft yield (%G.Y.), homopolymer

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(%H.P.), and total conversion (%T.C.). This monomer was selected because it is water soluble and, when grafted onto the chitosan, is expected to increase the hydrophilicity. These graft products may find use as textile finishes to enhance the hydrophilicity of synthetic fibers.

## EXPERIMENTAL

### Materials

Chitosan was obtained from Natural Biopolymer, Inc. (Redmond, WA). Its degree of deacetylation and the apparent viscosity were determined as 83.5% and 1133 MPa/s, respectively. Hydroxyethylmethacrylate (HEMA) from Sigma Chemical Co. (St. Louis, MO) was used as received, without further purification. Other chemicals such as potassium bromate, potassium bromide, potassium iodide, sodium hydroxide, formic acid, and carbon disulfide were used as received from Fisher Scientific (Springfield, NJ).

### Chitosan–Thiocarbonate

Chitosan was placed into a glass vessel containing sodium hydroxide solution [0–3% on weight of chitosan (owc)]. The reaction temperature was kept at 30°C using a thermostatic water bath throughout the process of thiocarbonation. A definite amount of carbon disulfide (0–4% owc) was added to the suspension and the contents were subjected to continuous stirring for 1 h. At the end of the reaction, chitosan–thiocarbonate was filtered and then washed with distilled water.

### Preparation of Chitosan–Poly(HEMA) Composite

Chitosan thiocarbonate was placed into a glass vessel containing a definite amount of HEMA (25–150% owc) and water, with continuous stirring, followed by addition of formic acid (0.5–2.5 g/g chitosan) and potassium bromate (0.2–0.8 mM/g chitosan), respectively. The material-to-liquor (M/L) ratio was kept at 1 : 30 and the polymerization temperature was varied from 30 to 60°C.

### Separation of Grafted Chitosan–Poly(HEMA)

The grafted chitosan was separated in a sodium hydroxide solution, filtered, and washed several times until pH 7 was reached. Finally, the grafted chitosan–poly(HEMA) was washed with water/

ethanol solution and dried at ambient temperature.

### Characterization of the Chitosan–Poly(HEMA) Composite

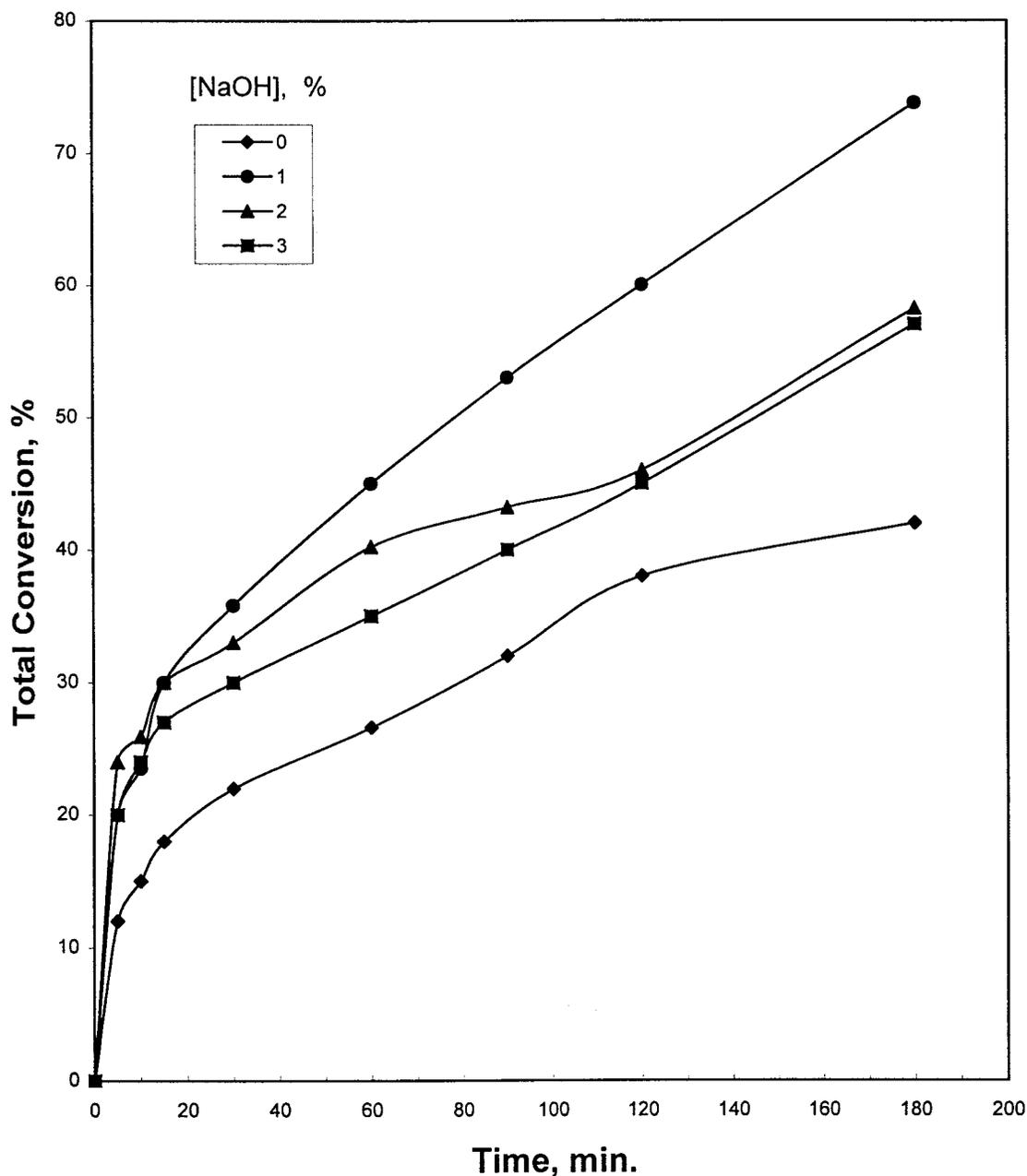
The percentage total conversion (%T.C.) was calculated by quantitative estimation of HEMA double bonds, according to a method reported by Wallace.<sup>20</sup> The percentage graft yield (%G.Y.) was determined by measuring the nitrogen content of the separated grafted chitosan according to the method of Kjieldal.<sup>21</sup> The homopolymer percentage (%H.P.) was determined by calculation based on %T.C. and %G.Y.

The apparent viscosity of the chitosan–poly(HEMA) composite (3%) was measured using a Brookfield RVT viscometer (Brookfield Instruments, Middleboro, MA) at 30°C. The term *composite* refers to the polymerization product, including unreacted chitosan, chitosan–poly(HEMA) graft copolymer, homopolymer, and oxidized chitosan. Infrared spectra of chitosan and grafted chitosan films of different HEMA contents were recorded on a Nicolet 510P FTIR spectrophotometer (Nicolet Instruments, Madison, WI). A new peak was observed in the chitosan–poly(HEMA) graft copolymer at 1724.9 cm<sup>-1</sup>, indicating the presence of methacrylate ester.

## RESULTS AND DISCUSSION

### Tentative Polymerization Mechanism

Thiocarbonation–potassium bromate initiation was previously reported to form an effective redox system capable of initiating grafting of different vinyl monomers onto polysaccharides such as starch, cellulose, and chitosan.<sup>22,23</sup> Potassium bromate is a powerful oxidizing agent, especially in strong acid medium. Moreover, because of the presence of the amino group on the chitosan backbone, unmodified chitosan has a reduction power as a result of contamination by different transition metals adsorbed on the chitosan during its preparation.<sup>24</sup> However, chitosan thiocarbonate has a higher reduction level than that of chitosan. Thus, when KBrO<sub>3</sub> (oxidant) is coupled with chitosan thiocarbonate (reductant), a very efficient redox-initiation system is established. In this system, the KBrO<sub>3</sub> acts a multiequivalent oxidant. Each bromate abstracts six hydrogen atoms from the (–SH) groups placed along the chitosan back-

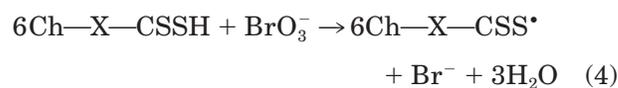


**Figure 1** Effect of [NaOH] on percentage total conversion. Thiocarbonation conditions:  $[\text{CS}_2] = 2\%$ , M/L ratio 1 : 20;  $30^\circ\text{C}$ , 1 h. Grafting conditions:  $[\text{KBrO}_3] = 0.6$  mmol/g chitosan,  $[\text{FA}] = 2$  g/g chitosan;  $[\text{HEMA}] = 75\%$ ; M/L ratio 1 : 30;  $40^\circ\text{C}$ .

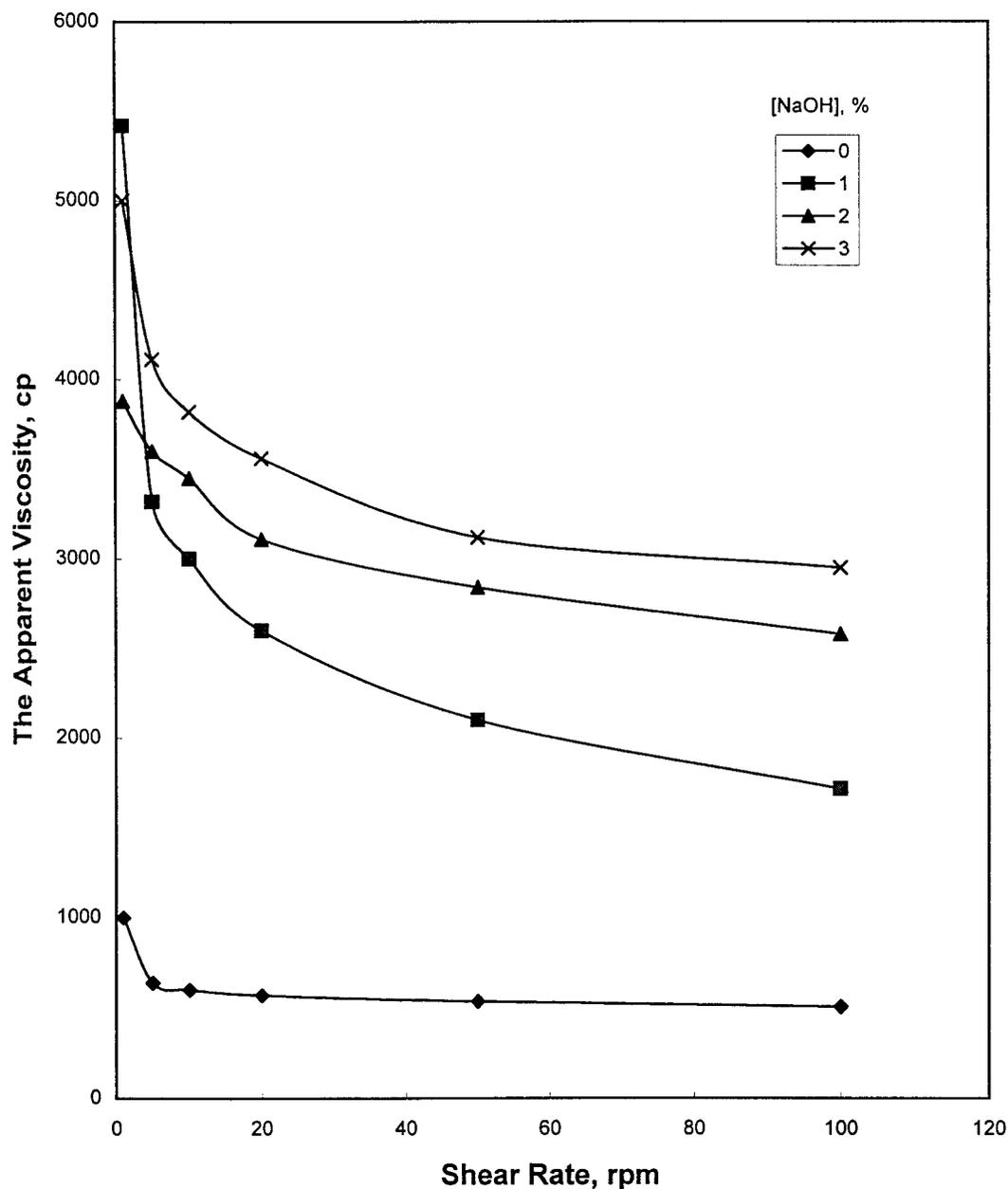
bone. Because chitosan–thiocarbonate is unstable, it decomposes rapidly to generate stable chitosan macroradicals. These radicals are capable of initiating vinyl grafting reaction onto chitosan.



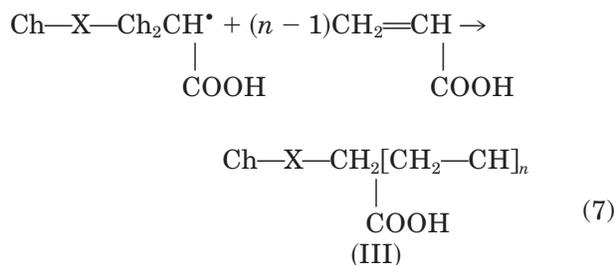
where Ch–X is chitosan and X is NH or O group.



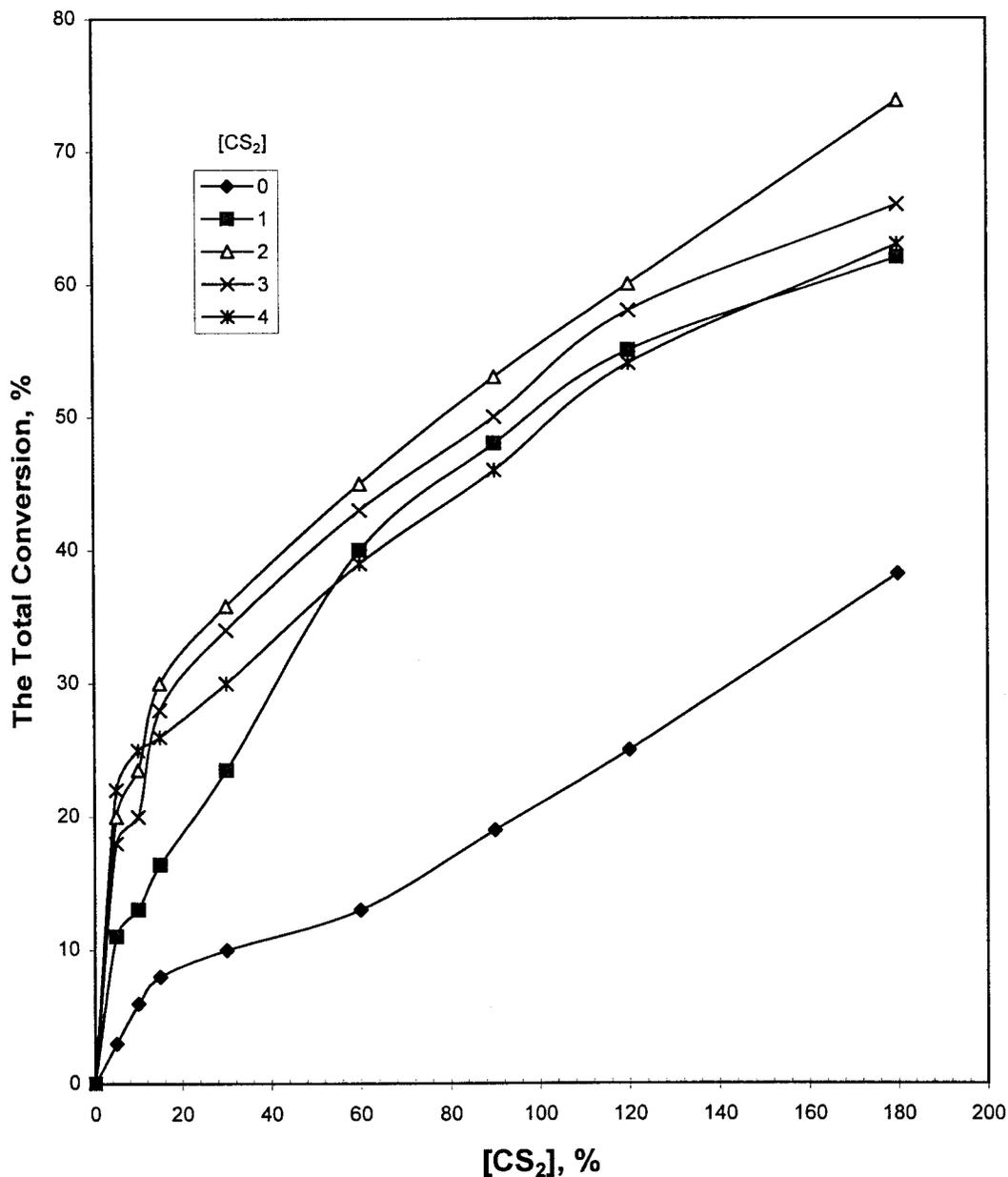




**Figure 3** Effect of [NaOH] on the apparent viscosity. Thiocarbonation conditions and grafting conditions are the same as in Figure 1.



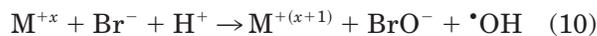
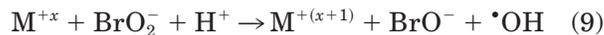
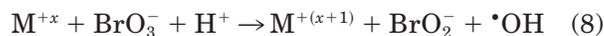
The propagating chains of chitosan may be terminated by two possible routes, disproportionation and/or recombination between two growing chitosan-poly(HEMA) macroradicals. The propagating chains of chitosan may also be terminated by reacting with any active sites present in the polymerization medium, such as a by-product of the redox reaction.<sup>25</sup> Homopolymerization of HEMA



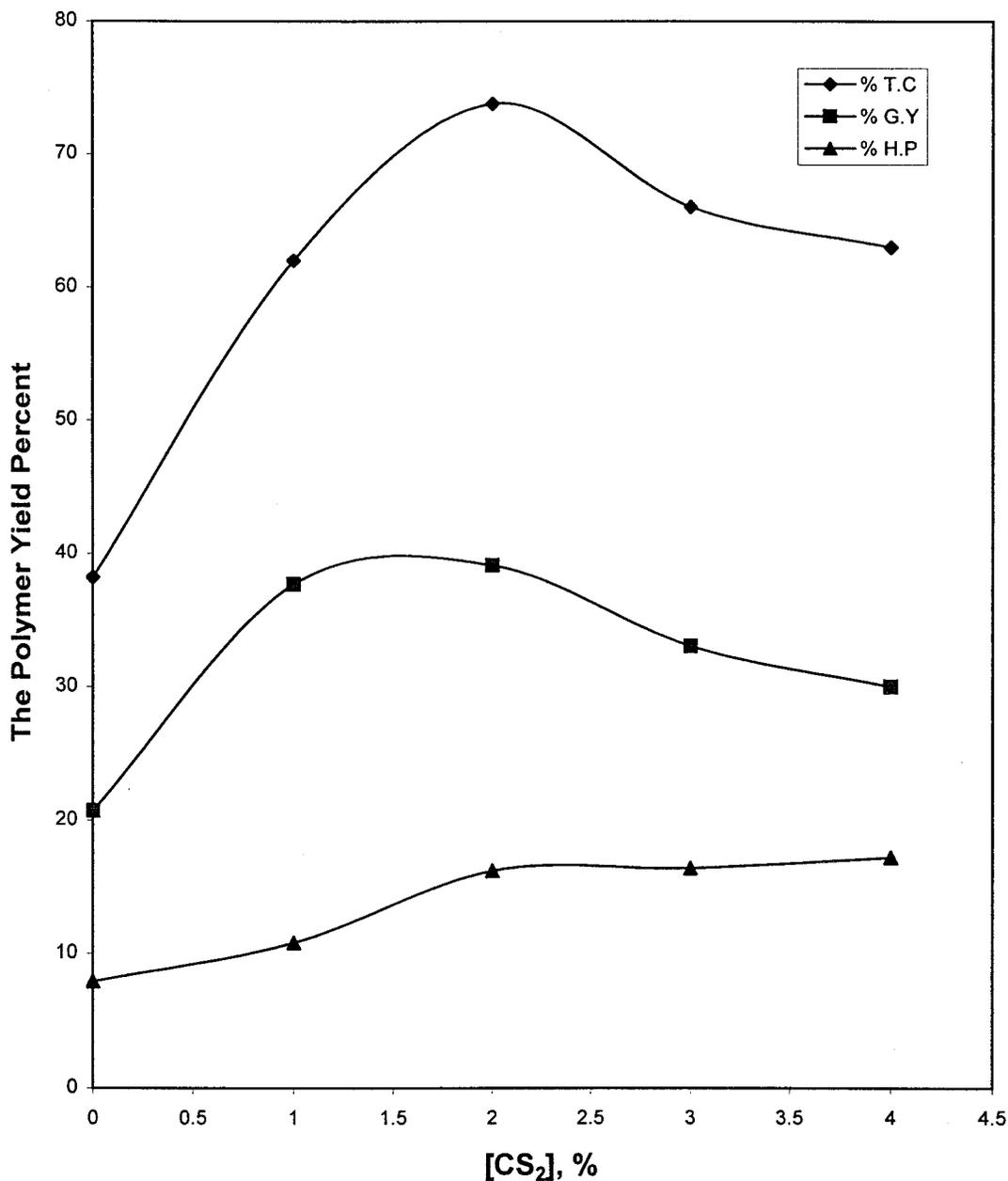
**Figure 4** Effect of  $[CS_2]$  on percentage total conversion. Thiocarbonation conditions:  $[NaOH] = 1\%$ , M/L ratio 1 : 20;  $30^\circ C$ , 1 h. Grafting conditions:  $[KBrO_3] = 0.6$  mmol/g chitosan,  $[FA] = 2$  g/g chitosan;  $[HEMA] = 75\%$ ; M/L ratio 1 : 30;  $40^\circ C$ .

may be carried out as a result of the reaction of the chitosan macroradical with water to generate hydroxyl radicals, which homopolymerize HEMA.

It is further reported that chitosan readily forms complexes with transition-metal ions and other heavy-metal ions during its preparation.<sup>24</sup> Thus  $KBrO_3$  alone may induce vinyl polymerization with chitosan, provided that the latter is contaminated with traces of transition metals as per the following mechanisms<sup>26</sup>:



The hydroxyl radicals may attack the chitosan macroradicals as well as HEMA, ultimately giving rise to graft copolymer and homopolymer.



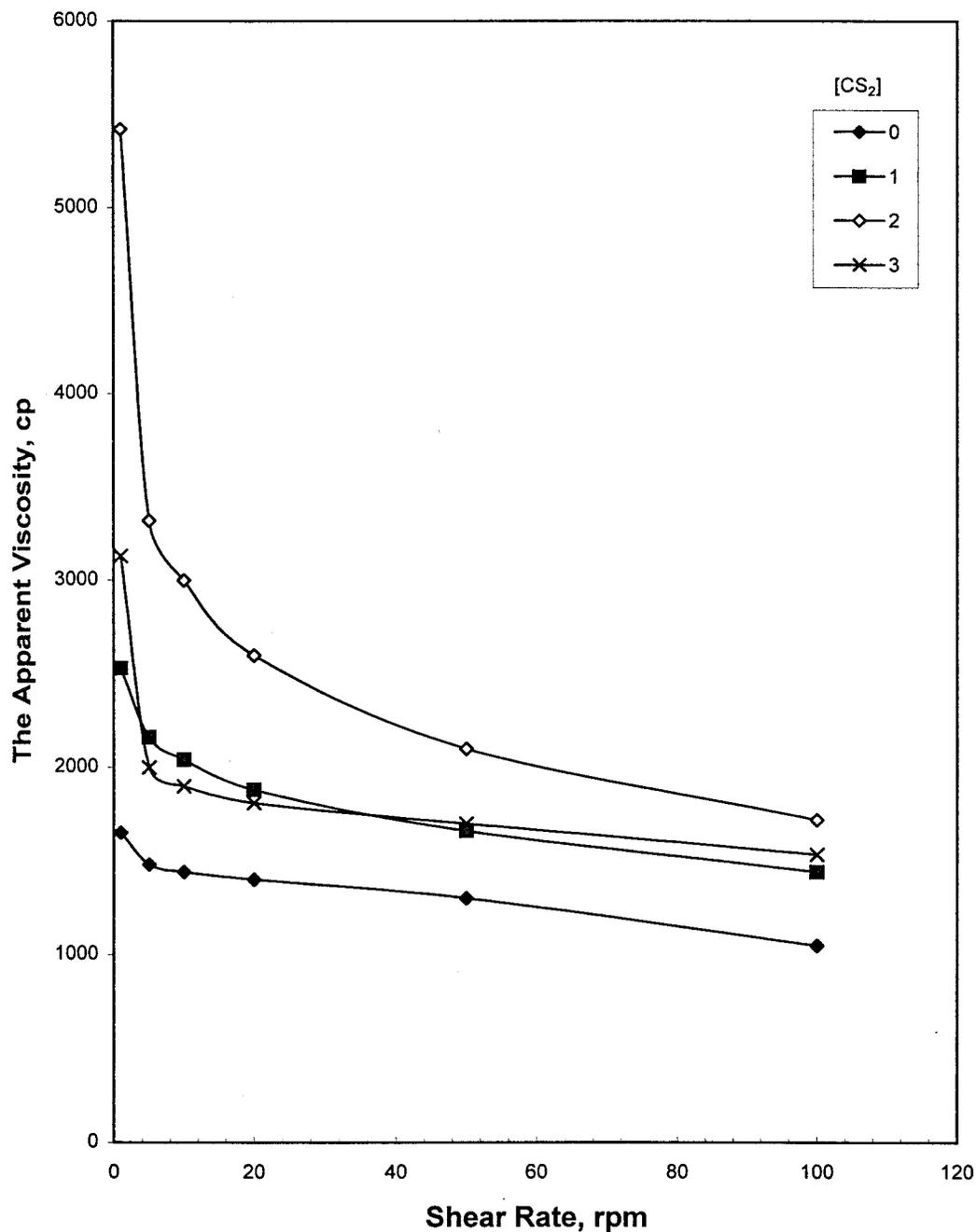
**Figure 5** Effect of  $[CS_2]$  on percentage polymer yield. Thiocarbonation conditions and grafting conditions are the same as in Figure 4.

Besides its ability to form chitosan macroradicals, bromate may also attack the chitosan glucosamine repeat unit at various positions. This results in the formation of oxidized chitosan and bromous acid, the latter of which may again attack the chitosan chains to give more oxidized chitosan derivatives. Taking the preceding mechanisms into consideration, we set out to study the factors affecting the preparation of chitosan-poly-(HEMA) composite.

#### Concentration Effects of the Thiocarbonation Component

##### *Concentration of Sodium Hydroxide*

Figure 1 shows the relation between the extent and rate of polymerization of hydroxyethyl-methacrylate (HEMA), expressed as percentage total conversion and NaOH concentration (0–3%). The thiocarbonation was carried out using 2%  $CS_2$ , a M/L of 1 : 20 and a temperature of 30°C for



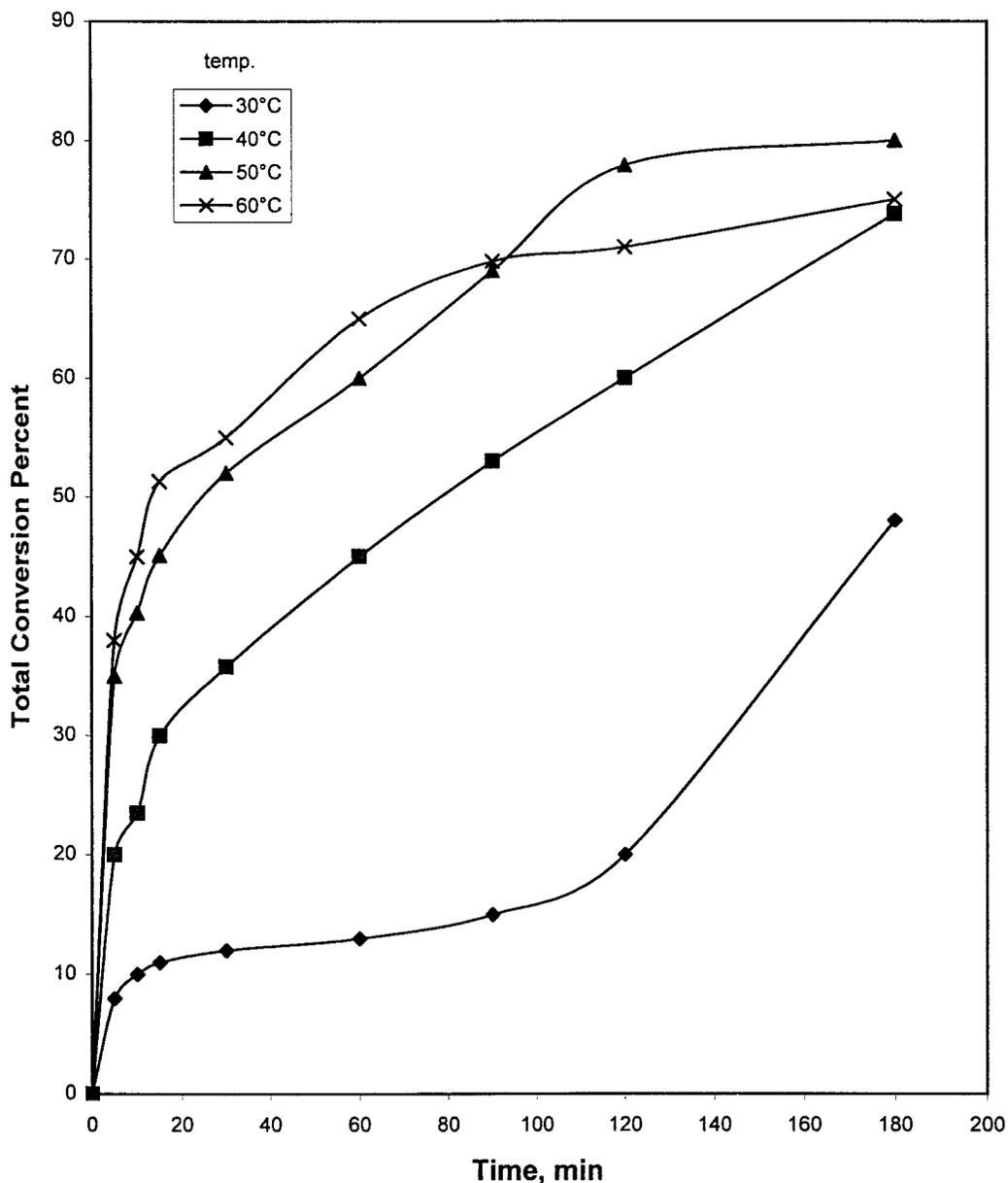
**Figure 6** Effect of  $[CS_2]$  on the apparent viscosity. Thiocarbonation conditions and grafting conditions are the same as in Figure 4.

1 h. The polymerization of HEMA onto chitosan was carried out using 6 mmol  $KBrO_3$ , o/wc, and HEMA (75% o/wc) at  $40^\circ C$  for various periods of time using a M/L ratio of 1 : 30.

It is clear that the total conversion of HEMA increases by increasing NaOH concentration in the range of 0–1%, o/wc, and a further increase above this limit is accompanied by a decrease in

the %T.C. of HEMA. Whatever the concentration of NaOH, the total conversion percentage increases as the duration of the polymerization time increases up to 180 min.

We should keep in mind that the efficiency of the polymerization reaction is highly dependent on the thiocarbonation process (reductant). This is determined by the concentration ratio of both

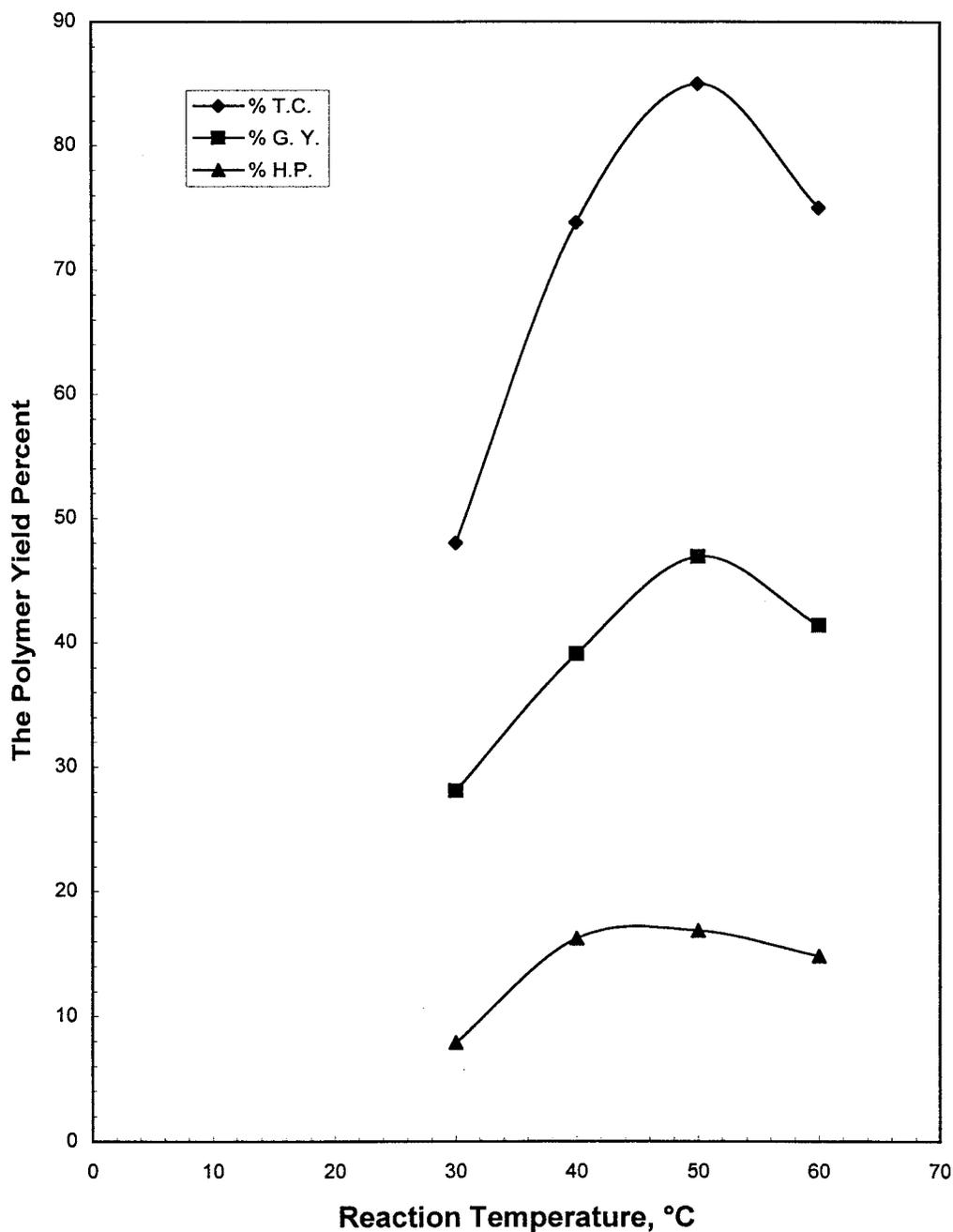


**Figure 7** Effect of reaction temperature on percentage total conversion. Thiocarbonation conditions:  $[\text{NaOH}] = 1\%$ ;  $[\text{CS}_2] = 2\%$ ; M/L ratio 1 : 20;  $30^\circ\text{C}$ , 1 h. Grafting conditions:  $[\text{KBrO}_3] = 0.6 \text{ mmol/g chitosan}$ ,  $[\text{FA}] = 2 \text{ g/g chitosan}$ ;  $[\text{HEMA}] = 75\%$ ; M/L ratio 1 : 30;  $40^\circ\text{C}$ .

NaOH and carbon disulfide during the thiocarbonation process, so increasing NaOH concentration in the range of 0–1% is accompanied by an increase in the reduction power of chitosan thiocarbonate and consequently enhances the reduction power of the whole polymerization reaction. When chitosan thiocarbonate is coupled with  $\text{KBrO}_3$ , a very efficient redox system is obtained. The polymerization reaction proceeds even in the

absence of NaOH because the chitosan has basic properties as a result of the presence of the amino groups along the chitosan backbone. Trace heavy-metal contaminants chelated to chitosan may induce polymerization.

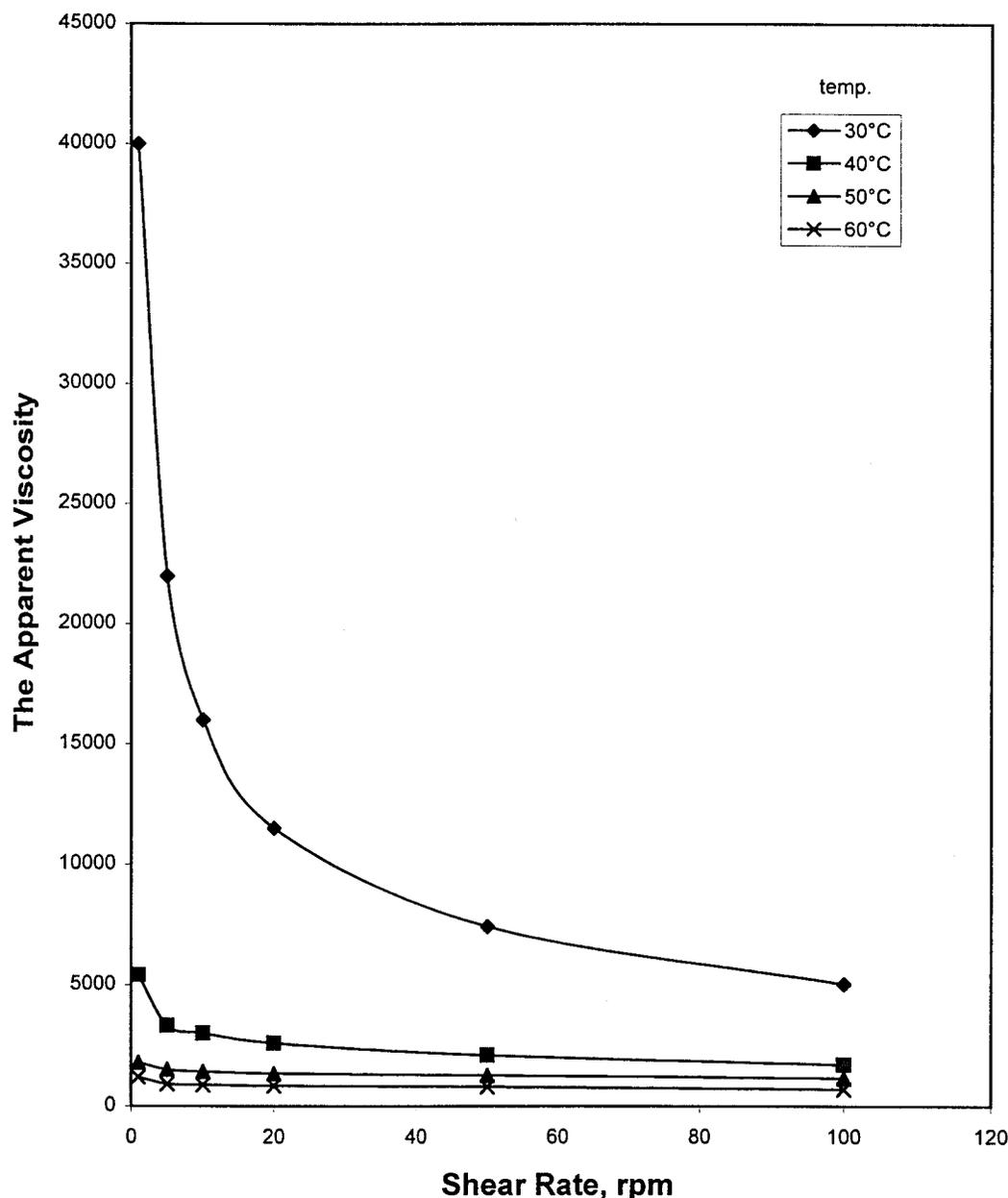
Figure 2 shows the effect of NaOH concentration on the final polymer yield percentage. It is clear that the polymer yield [i.e., percentage graft yield (%G.Y.), percentage homopolymer (%H.P.),



**Figure 8** Effect of reaction temperature on percentage polymer yield. Thiocarbonation conditions and grafting conditions are the same as in Figure 7.

and percentage total conversion (%T.C.)] increases with NaOH concentration up to 1%. Above this concentration, the polymer yield decreases significantly. The enhancement in the graft yield may be related to the increase in the number of active free radicals created along the chitosan backbone as a result of the increase in the concentration of NaOH.

Figure 3 shows the effect of NaOH concentration on the apparent viscosity of the polymerization products taken together as a whole, that is, the composite. The apparent viscosity was measured at 30°C and at different rates of shear. It is clear that the apparent viscosity increases sharply as the concentration of NaOH increases in the range 0–1%, which reflects



**Figure 9** Effect of reaction temperature on the apparent viscosity. Thiocarbonation conditions and grafting conditions are the same as in Figure 7.

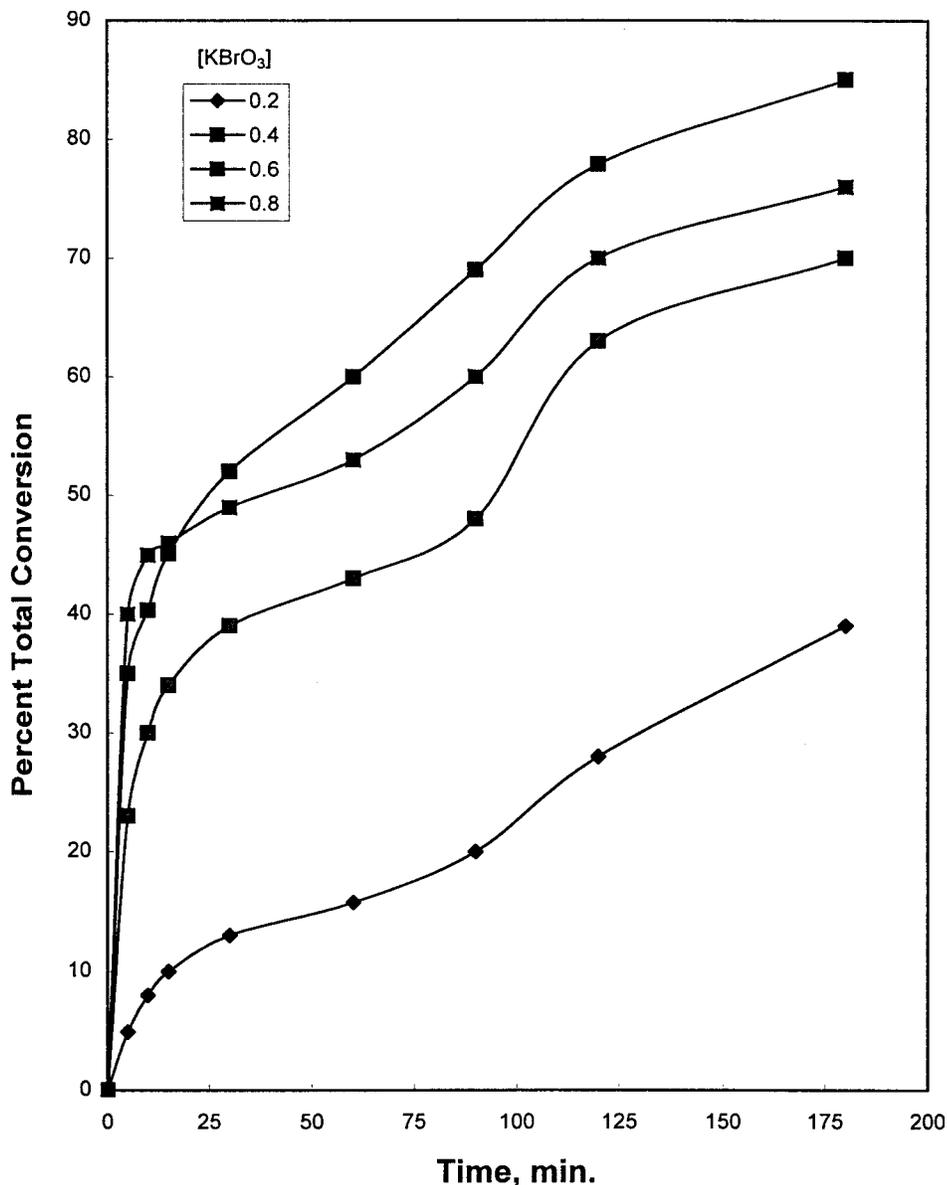
the high efficiency of the polymerization reaction.

#### *Concentration of Carbon Disulfide*

Figure 4 shows the effect of  $\text{CS}_2$  concentration (0–4%) on the rate and extent of the polymerization of HEMA, expressed as percentage total conversion, when  $\text{CS}_2$  was used along with NaOH solution (1%) in the thiocarbonation of chitosan. The polymerization reaction was carried out us-

ing 0.6 mM  $\text{KBrO}_3$ , o/wc, M/L ratio 1 : 30, and HEMA 75% at 40°C.

It is clear (Fig. 4) that the total conversion of HEMA increases by increasing concentration of  $\text{CS}_2$  in the range 0–2%, although a further increase is accompanied by a marginal decrease in the total conversion percentage. The enhancement in the %T.C. may be ascribed to the  $\text{CS}_2$  concentration increase from 0 to 2%, where the number of hydrosulfide groups created along the



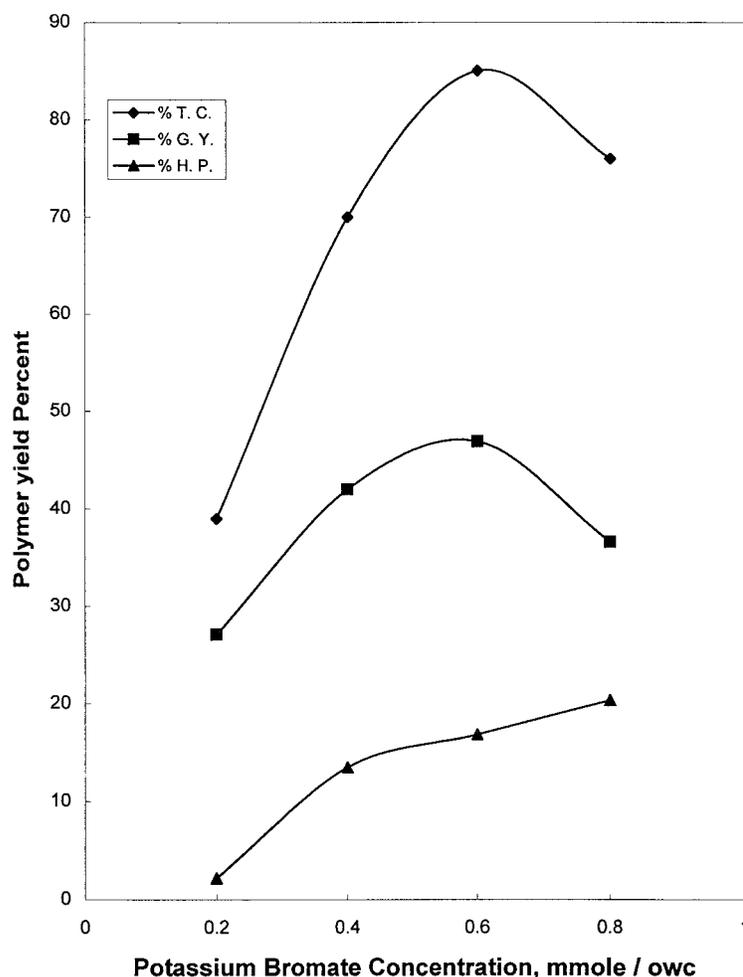
**Figure 10** Effect of  $[\text{KBrO}_3]$  on percentage total conversion. Thiocarbonation conditions:  $[\text{NaOH}] = 1\%$ ;  $[\text{CS}_2] = 2\%$ ; M/L ratio 1 : 20;  $30^\circ\text{C}$ , 1 h. Grafting conditions:  $[\text{FA}] = 2 \text{ g/g}$  chitosan;  $[\text{HEMA}] = 75\%$ ; M/L ratio 1 : 30;  $50^\circ\text{C}$ .

chitosan backbone increases and, consequently, the reduction power of the redox reaction. However, the decrement in the total conversion may be the result of the increase in the number of free radicals (above optimum limit) in the polymerization medium and, consequently, an increase in the possibility of recombination between the propagating chains.

Figure 5 shows the dependence of the polymer yield (including %G.Y., %H.P., and %T.C.) on the  $\text{CS}_2$  concentration. It is evident that both %T.C.

and %G.Y. increase as the concentration of  $\text{CS}_2$  increases in the range of 0–2%; a further increase above this limit is accompanied by a decrease in the total conversion and graft yield percentages. The %H.P. increases by increasing the  $\text{CS}_2$  concentration. As we described earlier, the efficiency of the polymerization reaction is strongly bounded by the efficiency of the thiocarbonation process.

Figure 6 shows the variation of the apparent viscosity of chitosan–poly(HEMA) composite with



**Figure 11** Effect of  $[\text{KBrO}_3]$  on percentage polymer yield. Thiocarbonation conditions and grafting conditions are the same as in Figure 10.

$\text{CS}_2$  concentration, when the viscosity is measured at different shear rates. It is seen that the apparent viscosity of the composite samples increases as the concentration of  $\text{CS}_2$  increases from 0 to 2% in the polymerization medium. This may be attributed to the formation of polymerized side chains of HEMA with high molecular weight. A further increase of  $\text{CS}_2$  concentration is accompanied by a decrease in the apparent viscosity. Such a decrease in the viscosity may be related to the formation of a large number of growing chains with low molecular weight and the increase in the oxidation power of the redox reaction as a result of the increase in the reduction power of the reductant.

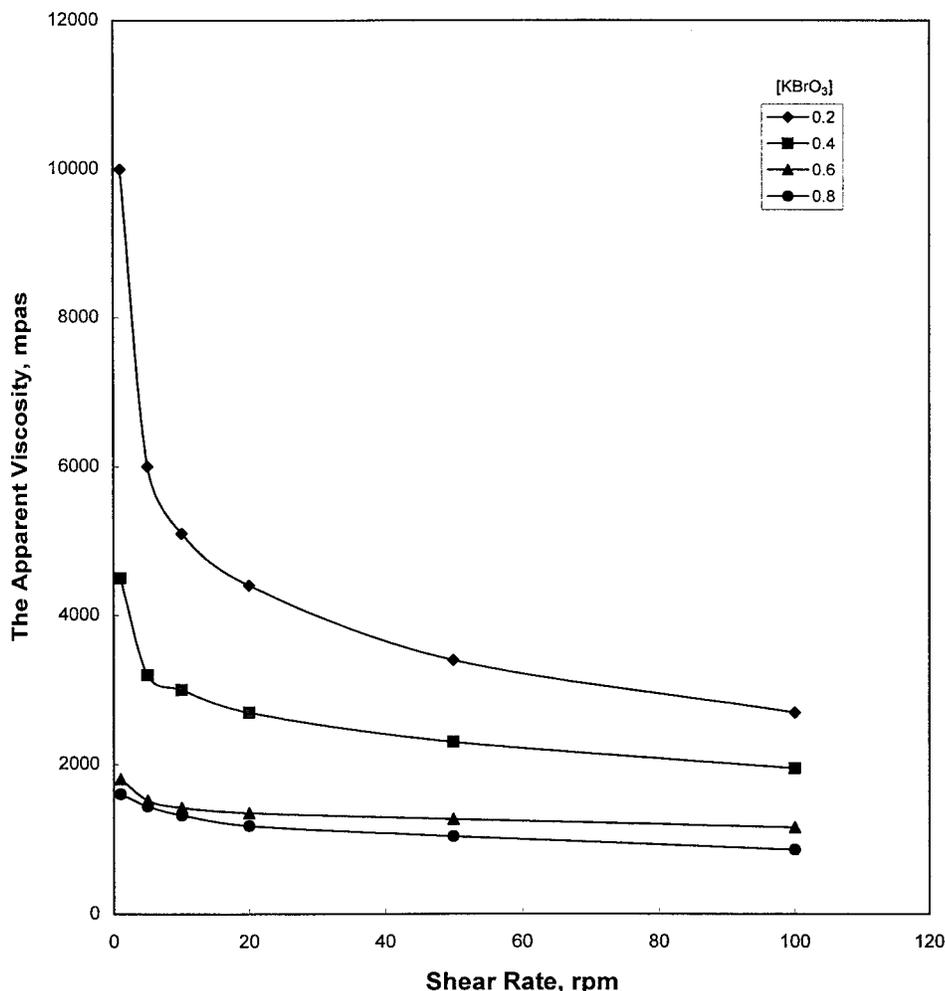
### Effects of Polymerization Conditions

#### *Effect of the Polymerization Temperature*

The reaction temperature plays an important role in the efficiency of polymerization processes as a

result of the influence of the activation energy on many aspects of the grafting reaction. Figure 7 shows the effect of the polymerization temperature on the extent and rate of polymerization of HEMA onto chitosan. The polymerization reaction was carried out at a temperature range of 30–60°C using 2 g of formic acid, 75% of HEMA, 0.6 mM of  $\text{KBrO}_3$ /1 g chitosan, and a M/L ratio of 1 : 30 was employed at constant thiocarbonation conditions of 2%  $\text{CS}_2$ , 1% NaOH, M/L ratio 1 : 20 at 30°C for 1 h. The results (Fig. 7) indicate that the effect of raising the polymerization temperature (from 30 to 50°C) is to bring about a significant increment in both the extent and the rate of the polymerization of HEMA.

Figure 8 shows the effect of temperature on the graft yield, homopolymer, and total conversion percentages when the polymerization reaction was conducted for 180 min. As evident, %G.Y., %H.P., and %T.C. increase as the polymerization



**Figure 12** Effect of  $[\text{KBrO}_3]$  on the apparent viscosity. Thiocarbonation conditions and grafting conditions are the same as in Figure 10.

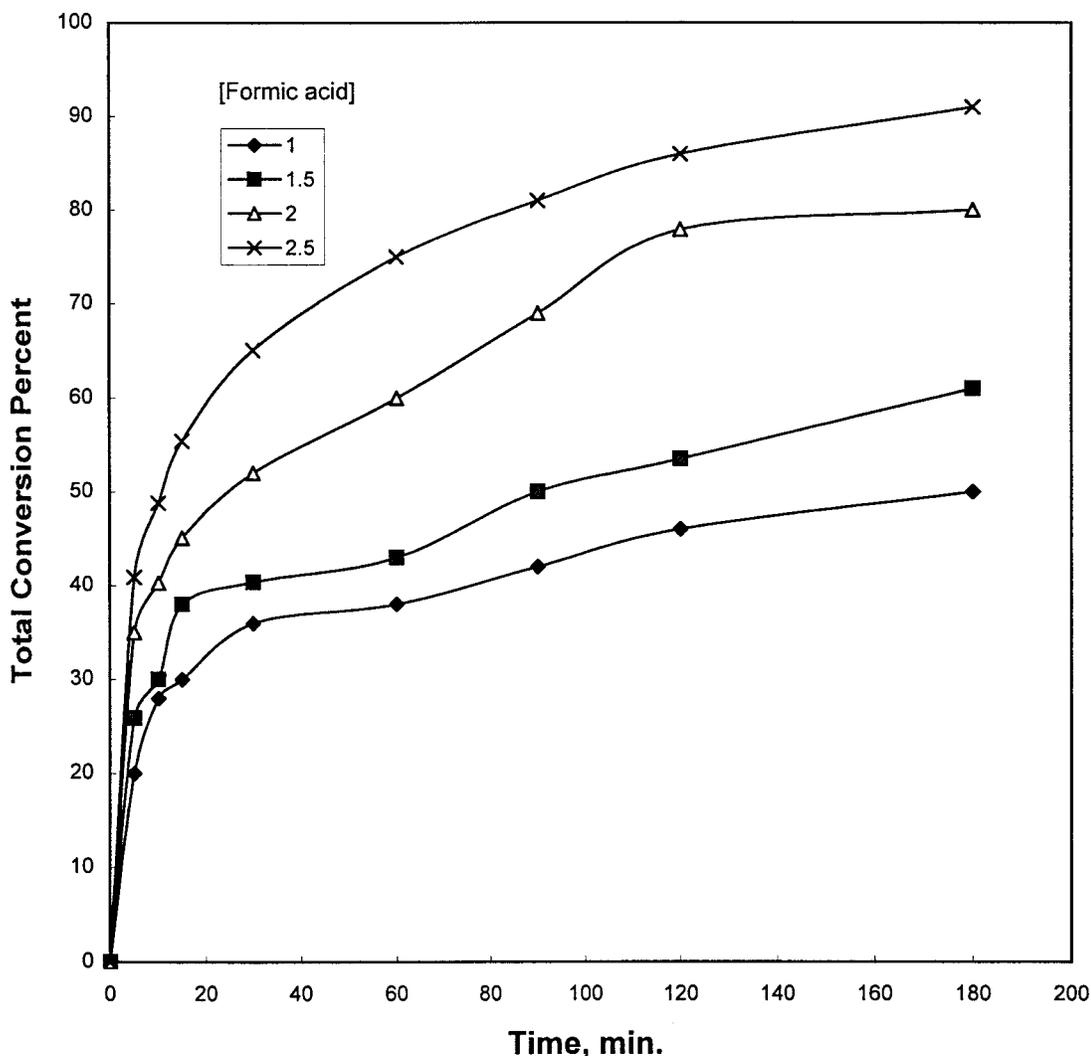
temperature rises in the range 30–50°C and then decreases by further increases in the reaction temperature. The enhancement in the polymer yield as a result of increasing the polymerization temperature could be ascribed to (1) reactant molecular mobility, (2) compatibility of the reactant ingredients, (3) enhanced disintegration of  $\text{KBrO}_3$ , (4) enhanced oxidation efficiency of  $\text{KBrO}_3$ , and (5) faster initiation and propagation reactions. However, the decrement in the polymer yield may be attributed to an increase in the recombination of the free-radical propagating chains.

Figure 9 reflects the correlation between the apparent viscosity of chitosan–poly(HEMA) composite and the polymerization temperature. For a given rate of shear, the apparent viscosity decreases as the reaction temperature rises. Such a decrease in the apparent viscosity results from

the high oxidation efficiency of potassium bromate at higher temperatures and in the presence of base.

#### **Effect of Potassium Bromate Concentration**

Figure 10 shows the effect of potassium bromate concentration on both the extent and the rate of HEMA polymerization onto chitosan. It is seen that within the range studied, increasing  $\text{KBrO}_3$  concentration from 0.2 to 0.6 mM is accompanied by an increment in the total conversion percentage, but beyond this concentration, the %T.C. decreases gradually. This is interpreted in terms of the creation of more active free-radical species, which contribute largely to the initiation and propagation of the polymerization via grafting of HEMA onto chitosan as well as via homopolymer-



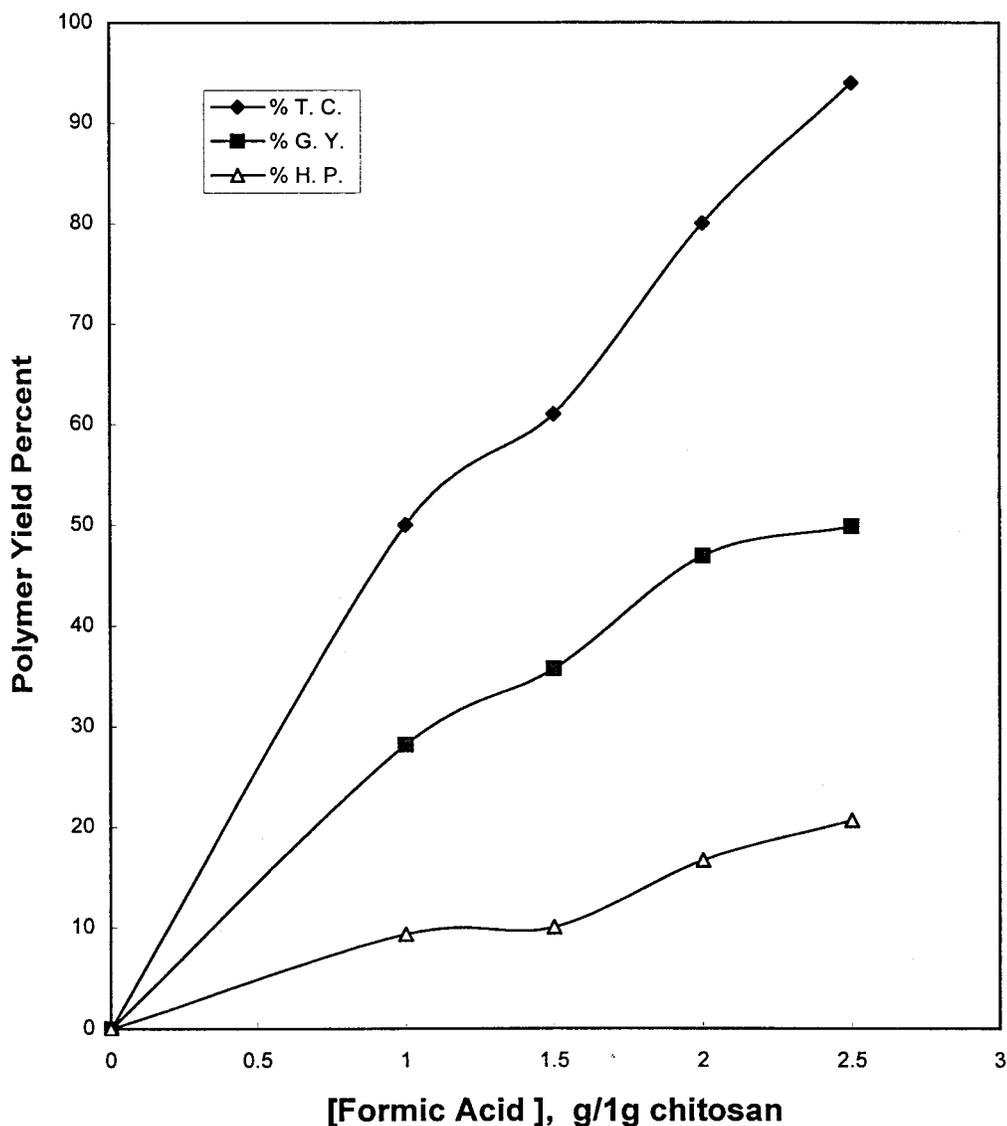
**Figure 13** Effect of [Formic Acid] on percentage total conversion. Thiocarbonation conditions: [NaOH] = 1%; [CS<sub>2</sub>] = 2%; M/L ratio 1 : 20; 30°C, 1 h. Grafting conditions: [KBrO<sub>3</sub>] = 0.6 mmol/g chitosan; [HEMA] = 75%; M/L ratio 1 : 30; 50°C.

ization. Considering the initiation mechanism postulated earlier, one realizes the role played by KBrO<sub>3</sub> in this mechanism and, therefore, the great dependence of the mechanism on KBrO<sub>3</sub> concentration.

Figure 11 shows the graft yield, homopolymer, and total conversion percentages as a function of KBrO<sub>3</sub> concentration. The results reveal, on the one hand, that the incorporation of KBrO<sub>3</sub> at concentration range 0.2–0.6 mM/1 g chitosan is accompanied by increasing polymer yield components (G.Y., H.P., and T.C.) but, on the other hand, beyond this concentration, the polymer yield decreases gradually, except the homopolymer percentage, which continues to rise. It is clear that, using 0.6 mM of KBrO<sub>3</sub>/1 g chitosan

represents the optimum conditions for the grafting reaction. The enhancement in the polymerization reaction at this critical concentration is explained in terms of the creation of larger amounts of free-radical species through the chitosan thiocarbonate–KBrO<sub>3</sub> redox system, as well as the reaction of bromate with traces of heavy metals contaminating chitosan, as shown earlier [eqs. (8)–(10)].

The preceding findings may be clarified in terms of the role played by the KBrO<sub>3</sub> during the polymerization reaction. It is reasonable to assume that the role of KBrO<sub>3</sub> during the polymerization involves different chemical features, that is, it acts as a free-radical generator, bromine generator, and chain terminator. We expect that



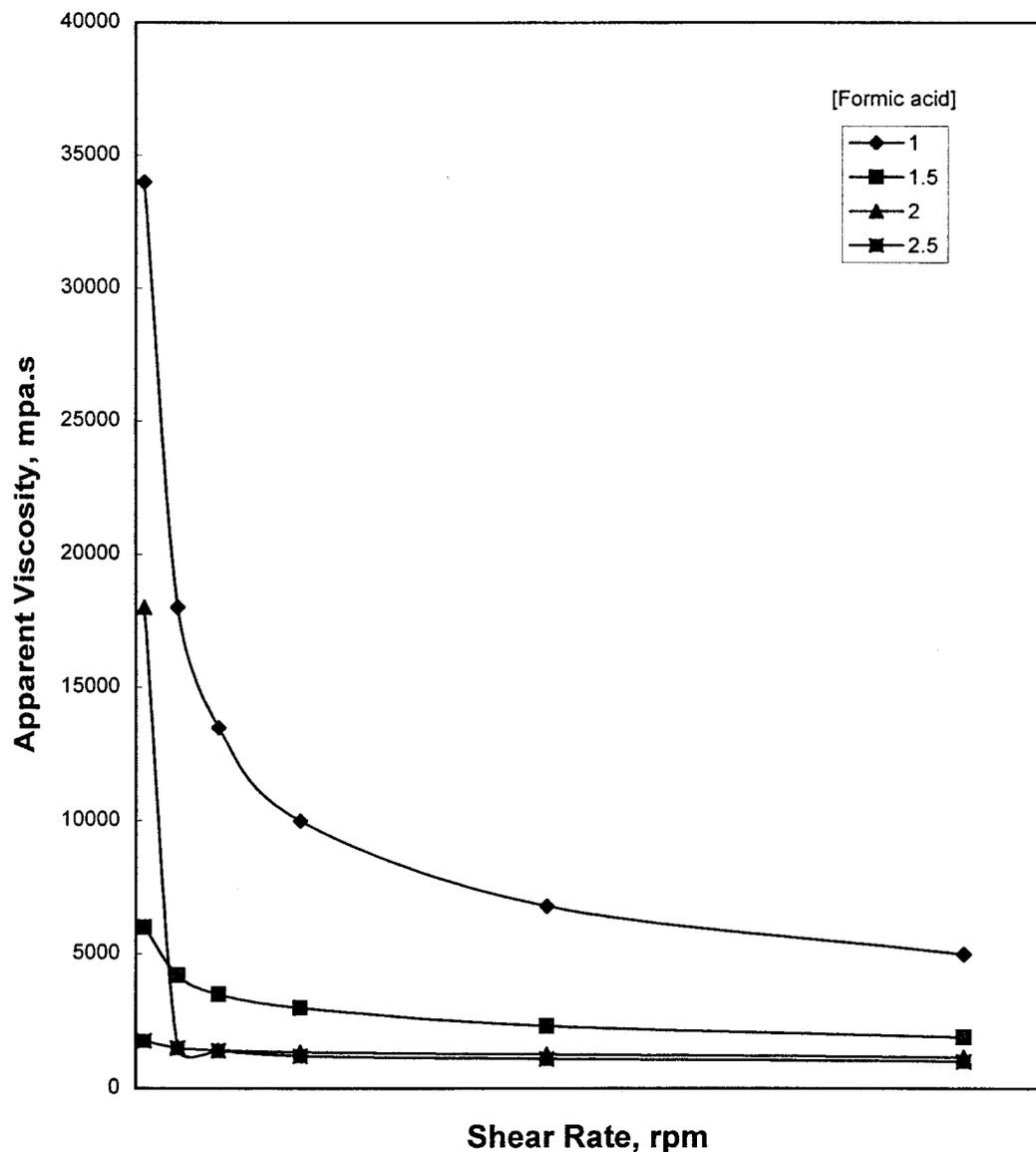
**Figure 14** Effect of [Formic Acid] on percentage polymer yield. Thiocarbonation conditions and grafting conditions are the same as in Figure 13.

each of these reactions has a different rate constant and activation energy; thus preeminence of one reaction over another would explain the difference in the behavior of the polymer yield with increasing  $\text{KBrO}_3$  concentration.

Figure 12 shows the correlation between the apparent viscosity of chitosan-poly(HEMA) composite and  $\text{KBrO}_3$  concentration in the polymerization medium is accompanied by a decrease in the apparent viscosity. This is not a surprise, but rather is expected, because the decrease in the apparent viscosity is the result of the degradation action of  $\text{KBrO}_3$  as well as the liberation of  $\text{Br}_2$  at higher concentrations of bromate, which may also degrade the chitosan chain.

#### *Effect of Formic Acid Concentration*

Figures 13 and 14 show the effect of the formic acid concentration, which is for the dissolution of chitosan and for keeping the polymerization medium in the acid range. This is shown as a function of extent and rate of polymerization of HEMA and polymer yield percentage. It is evident that both the total conversion and the polymer yield percentages increase by increasing the formic acid concentration. The enhancement in the polymerization reaction of HEMA by increasing the formic acid incorporated in the polymerization medium could be associated with (1) greater solubility of chitosan, thereby increasing the graft-

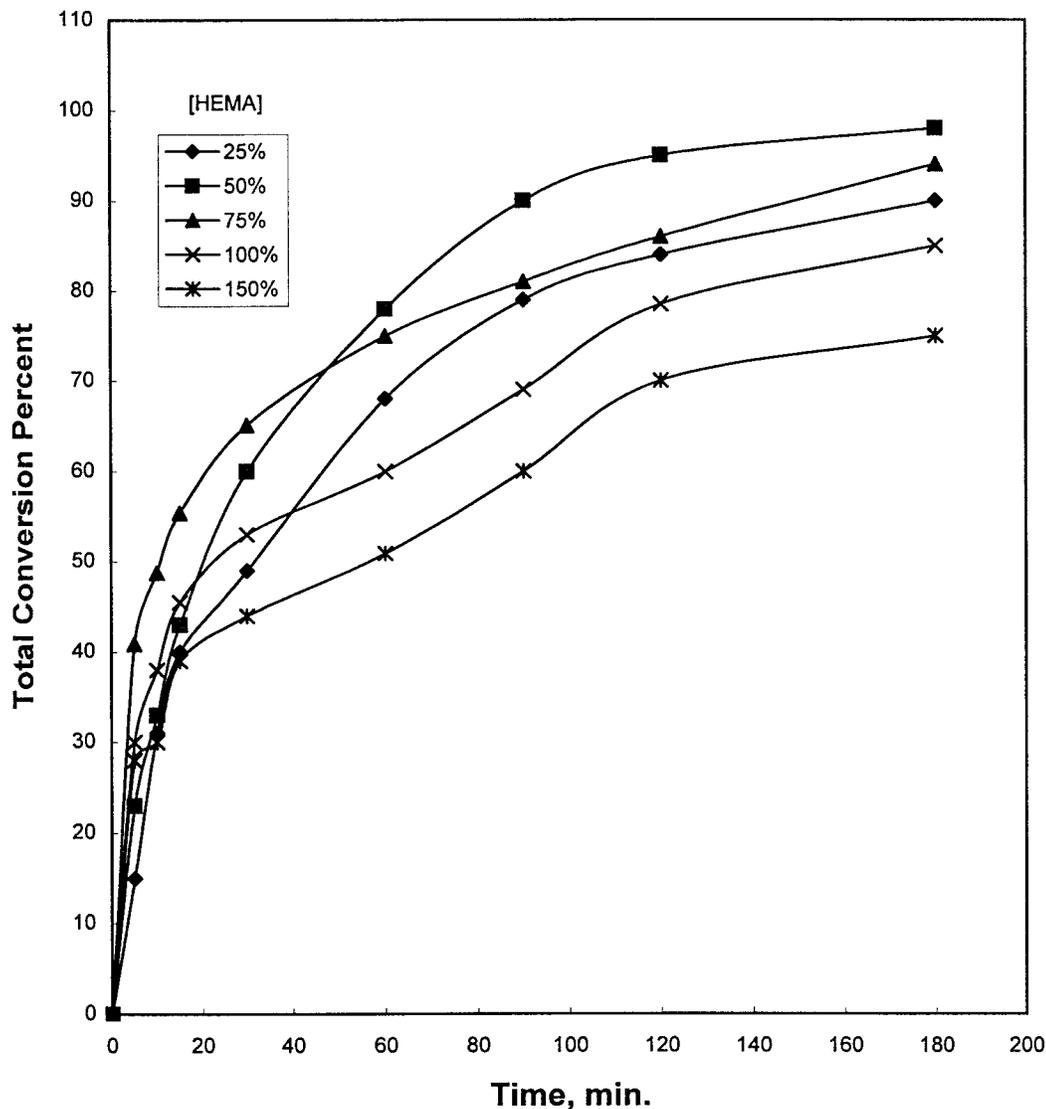


**Figure 15** Effect of [Formic Acid] on the apparent viscosity. Thiocarbonation conditions and grafting conditions are the same as in Figure 13.

ing and homopolymerization of HEMA; (2) decreasing the pH of the polymerization medium, which benefits the polymerization reaction; and (3) higher rate of decomposition of thiocarbonation-KBrO<sub>3</sub> redox system giving rise to an abundance of primary free-radical species that contribute to the initiation of the grafting and homopolymerization.

Figure 15 shows the effect of the formic acid concentration on the apparent viscosity of the whole polymerization product of chitosan-poly(HEMA) composite. The apparent viscosity was measured at 30°C under different rates of shear.

The decrement in the apparent viscosity by increasing the concentration of formic acid in the polymerization medium may be interpreted in terms of the molecular degradation of chitosan and the decrease of the molecular weight of poly(HEMA). Increasing the formic acid concentration is accompanied by an increase of free-radical species created by the faster decomposition rate of the thiocarbonation-KBrO<sub>3</sub> redox system in the polymerization medium. These free radicals seem to perform two other functions: (1) increasing termination of growing poly(HEMA) chains, thereby decreasing their molecular weight; and (2) oxidiz-



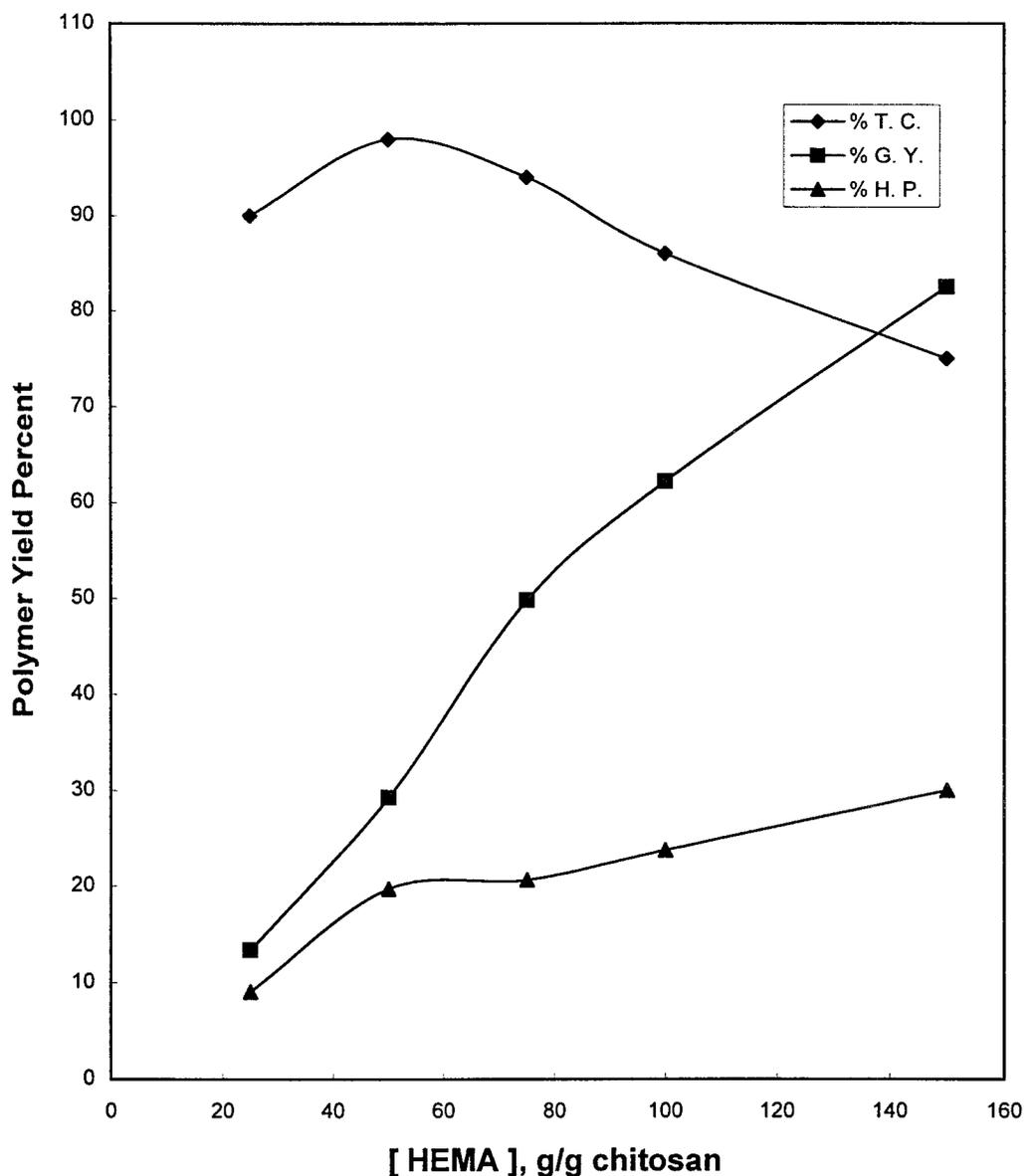
**Figure 16** Effect of [HEMA] on percentage total conversion. Thiocarbonation conditions: [NaOH] = 1%; [CS<sub>2</sub>] = 2%; M/L ratio 1 : 20; 30°C, 1 h. Grafting conditions: [KBrO<sub>3</sub>] = 0.6 mmol/g chitosan; [FA] = 2.5 g/g chitosan; M/L ratio 1 : 30; 50°C.

ing chitosan molecules to lower molecular weight. Both of these tendencies result in shorter chains, causing the decrease of apparent viscosity of the composite.

#### *Effect of HEMA Concentration*

Figure 16 shows the total conversion versus HEMA concentration. Total conversion is taken as a measure of the extent and rate of polymerization of HEMA with chitosan but also includes HEMA homopolymerization. The results imply that the total conversion percentage of HEMA increases as HEMA concentration increases in

the range 25–50%, based on weight of chitosan. Beyond this concentration, the total conversion decreases gradually. It may be that the conversion of HEMA monomer to poly(HEMA) at higher HEMA concentrations is accompanied by a portion of monomer, which most probably undergoes no reaction. However, it may be argued that the percentages of graft yield and homopolymer (shown in Fig. 17) are higher at higher concentration of HEMA. The presence of higher HEMA concentration in the polymerization medium provides greater availability of HEMA molecules to be present in the proximity of the immobile chi-



**Figure 17** Effect of [HEMA] on percentage polymer yield. Thiocarbonation conditions and grafting conditions are the same as in Figure 16.

tosan macroradicals, thus increasing grafting. The same holds true in the liquid phase of the polymerization system and accounts for the higher percentage of homopolymer at higher HEMA concentration. It seems likely that above a certain concentration, the HEMA monomer remains unreacted because of (1) the consumption of the initiator, (2) the change in the molecular structure of the reaction products as the polymerization proceeds, and (3) changes in the polymerization medium (reactant) by the presence of higher HEMA.

## CONCLUSIONS

Chitosan is efficiently grafted with hydroxyethyl-methacrylate (HEMA) using thiocarbonation-potassium bromate for redox initiation. A tentative polymerization mechanism is described, which accounts for many of the observed results. The effects of the reaction conditions and temperature were evaluated. Total conversion of HEMA monomer ranged up to 75%. A maximum graft yield of 38% on the chitosan was attained with the best reaction conditions. Homopolymer of HEMA

ranged from 2 to 16% on weight of the chitosan. The composite material was easily cast as films, which were featureless in the SEM.

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