4.1 Synthesis of poly($\in$-caprolactone)

The polymerization of poly($\in$-caprolactone) was initiated by triethyl aluminum. The initiator was obtained from the reaction of ethylmagnesium bromide and aluminum chloride. The procedure can be represent by the Scheme 4.1 as shown below;

$$CH_3CH_2Br + Mg \xrightarrow[\text{0 °C}]{\text{dry ether}} CH_3CH_2MgBr \xrightarrow[\text{dry ether, } N_2]{AlCl_3} Al(CH_2CH_3)_3$$

$$\underset{(CH_2)_5}{\overset{\overset{\displaystyle O}{\parallel}}{(C-O)}} \xrightarrow[\text{dry toluene, 85 °C, } N_2]{Al(CH_2CH_3)_3} \quad \overset{\overset{\displaystyle O}{\parallel}}{[-C-(CH_2)_5-]_n}$$

Scheme 4.1 The procedure for synthesis of poly($\in$-caprolactone)

From Tables 3.1 and 3.2, there exists no relationship between the ratio of monomer to initiator and the molecular weights of the obtained synthetic polymers. Since it is realized that if the smaller amount of the initiator is used, the higher molecular weights of polymers will be obtained. The

obtained results may be affected by the pyrolysis of $Al(CH_2CH_3)_3$. Some of organometallic compounds can undergo pyrolytic reaction in the presence of some oxidizing agents. Aluminium alkyls react readily with oxygen. The reaction can be violent if not controlled. Aluminum alkyls can also react with the compounds containing active hydrogen, e.g., water, acids, alcohols, primary amines and organic acids (60). Since the experiments were run in the less protective dry bag, the just previous mentioned reactions might make the initiator be inactive. It is believed that the true amount of the initiator presented in the reaction system is unequal to that of introduced one.

When no solvent was used (No. 3), the percentage yield is found to be remarkedly decreased. The results can be attributed to the diffusion of the initiator to monomer which is prohibited by viscous polymer solution in monomer, thus the unreacted monomer still remains in a significantly large amount. In addition, the growing polymer keeps monomer inside its so called " gel ", the phenomena of the encapsulation of monomer is well known as " gel effect ". By the phenomena, the encapsuled monomer is left to be free from catalyst attack and finally unreacted.

4.2 Graft copolymerization of methylacrylate onto starch

Since it is believed that the graft copolymers with high percentage grafting yield or grafting efficiency can be blended with other commercial synthetic polymers, in this research the optimum conditions for the grafting reaction were investigated. The factors which were determined for their effects were reaction volume, amount of ceric ion, amount of monomer, amount nitric acid and temperature. In preliminary study, it was found that method for the addition of initiator could effect the grafting reaction so the time-interval for the addition of initiator was also investigated. For each experiment the grafting parameters (see section 3.2.2.1) were calculated and plotted against the varied factors. At the condition which afforded the highest percentage grafting yield and grafting efficiency were considered to be the optimum condition for the grafting reaction. All these results are as follows:

4.2.1 Effect of variation of the reaction volumes

The results obtained when the reaction volumes, or in fact, the volumes of water, are varied are shown in Figure 4.1. and Table 3.3. When the reaction volumes are smaller, the concentrations of the suspending starch and monomer are higher, the chain growth reactions of grafted polymethylacrylate or the side chains growing undergo very quickly. The growing " hydrophobic " side chains may attach each other chemically, physically to form

Grafting parameters (%)

Reaction volume (ml)

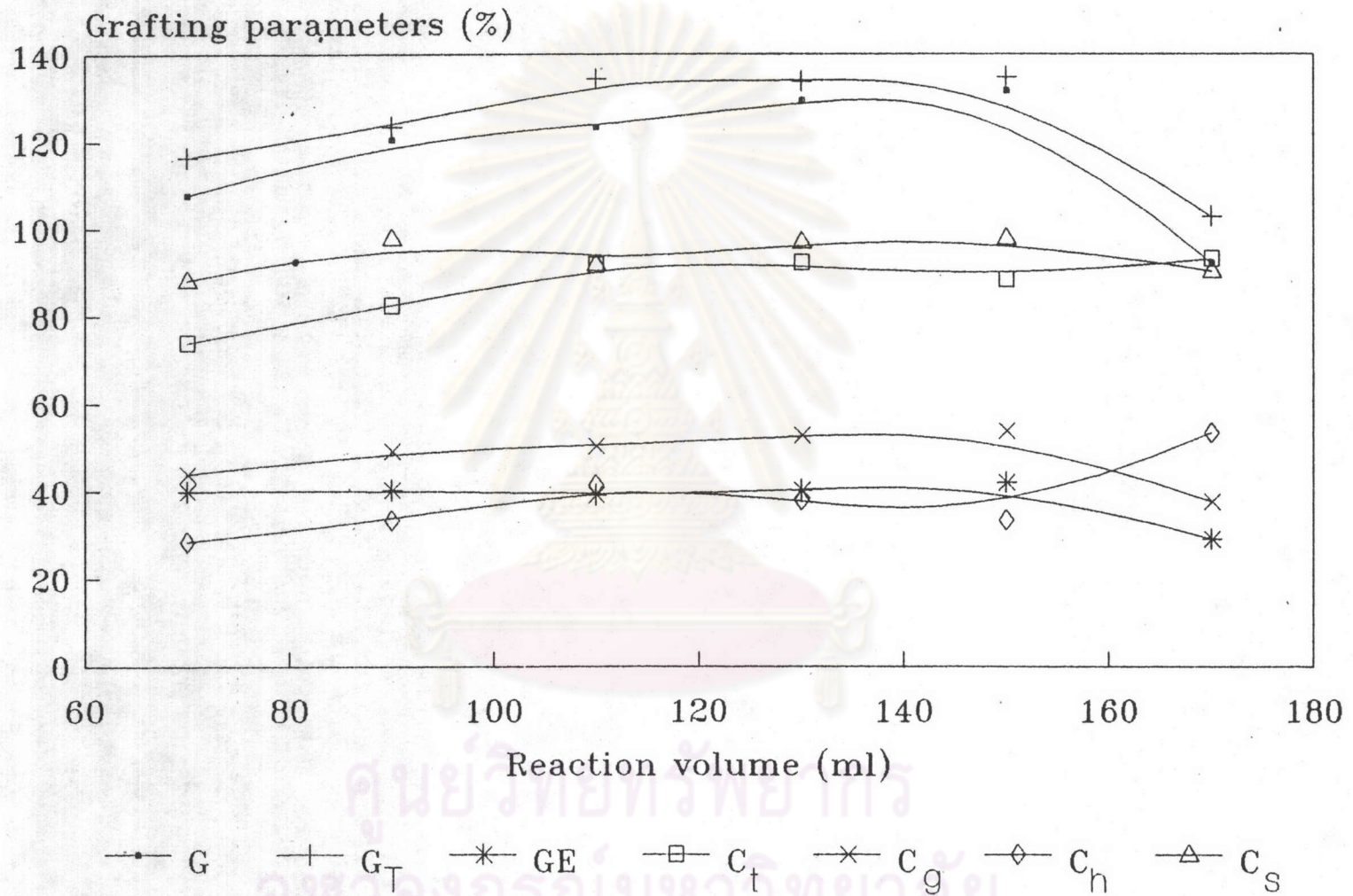G   G_T   GE   C_t   C_g   C_h   C_s

Figure 4.1 Plot of grafting parameters against the reaction volumes

a rubber-like lump in which unreacted monomer is absorbed. The low stirring speed is another factor that causes the formation of a rubber-like lump. This phenomenon prohibits further polymerization and thus the termination reaches its stage too early. Consequently, the total products are obtained with a low yield.

At the small reaction volume, the lower percentage grafting and grafting efficiency were obtained. (see Table 3.4) This can be explained that at the small reaction volume, the initiation to form starch radicals occured very quickly and followed by the grafting reaction readily. Finally, the fast termination stop the growing of the side chains and other reactions as the rubber-like lump is formed.

When the larger reaction volumes (beyond the critical the volume) are used, a smaller amount of starch radicals are formed because less opportunity for the starch molecule become contact with ceric ion. On contrary, the monomer which can be dissolved in water very well can readily react with ceric ion. At the same moment, the penetrating of Ce (IV) to monomer dissolved in aqueous phase to form monomer radicals becomes predominant. The side reaction of homopolymerization is realized to compete the propagation of grafting reactions. Under these conditions, though the high yield of total products is obtained since the reaction time is long enough for completing of all reactions in the system, the low yield of grafted products is

obtained.

At the appropriate reaction volume (140 ml), the formation of abundance of starch radicals is predominant over that of monomer radicals, so the system with the critical reaction volume gives higher yield of grafting product. The increase of reaction volumes up to the critical value gives another advantage "space" for growing hydrophobic chains to suspend without forming a ball-shaped product.

4.2.2 The time-intervals of the addition of the initiator

Figure 4.2 shows the obtained results which indicate that at the high speed of introduction, the formation of Ce (IV)-starch complex undergoes rapidly and then the dissociation of the complex gives abundant amount of starch radicals. The sudden increase of the radicals affects the yield of grafted products like the case with small reaction volume described in the section 4.2.1.   Thus the low yield of grafted products can be expected to obtain when the narrow time-intervals are used (Table 3.6).   The narrowest time-intervals which give high yield are preferred since they reduce the time spent for running the reactions.   In this study the time-interval of 15-mins is the suitable for addition of the initiator as can be seen in Figure 4.2.
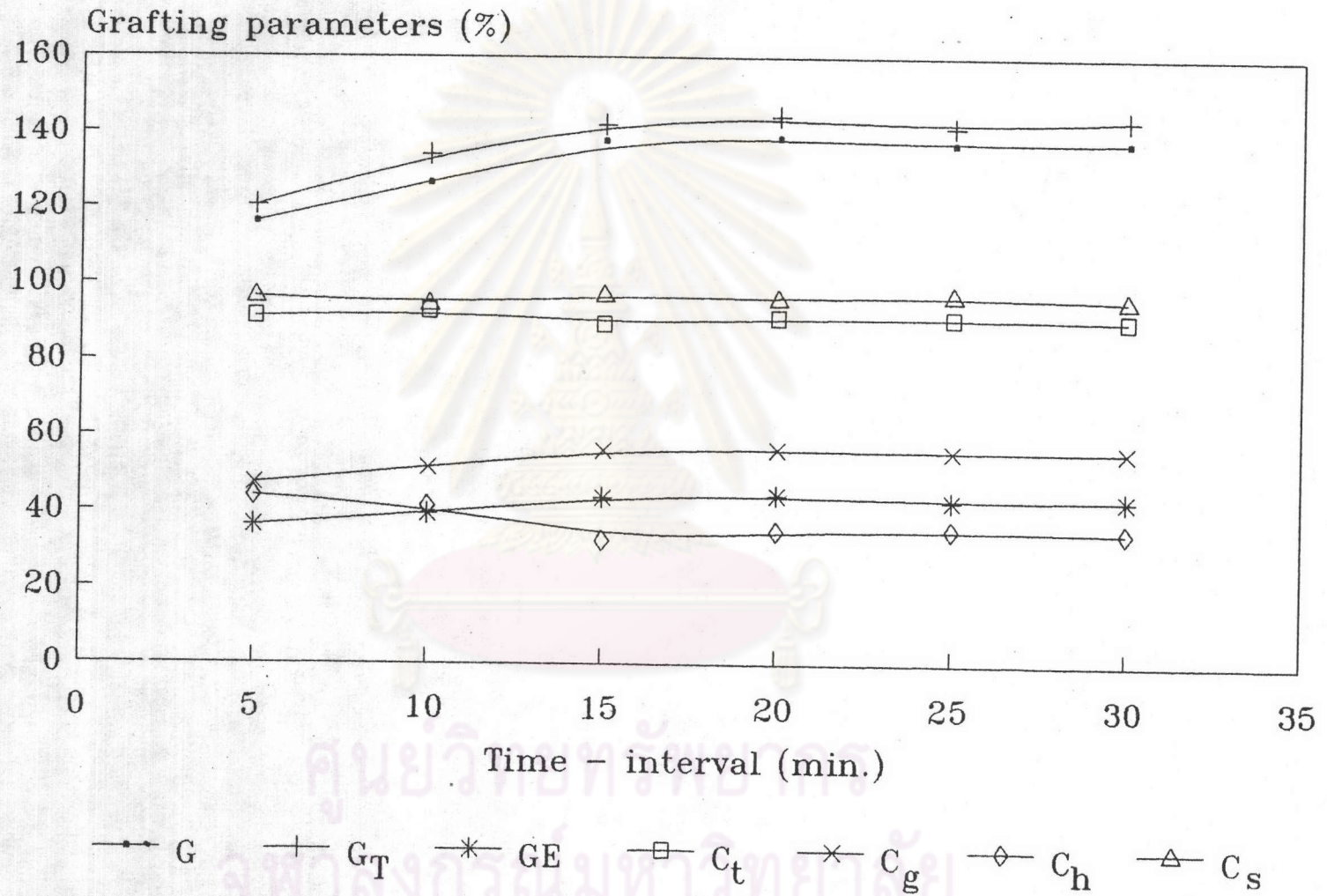
Figure 4.2 Effect of time-interval on grafting paramaters

4.2.3 Effect of variation of initiator

The increase of amount of ceric ion affects the rate of the reactions in which this ion is involved, such as generation of starch radicals, oxidation of starch radicals, termination of growing polymer chains, and initiation of homopolymerization. The percentage grafting and efficiency increase along with the increase of ceric ion up to the critical value (Table 3.8) because the formation of starch radicals has been increased. On the other hand, since at high amount of ceric ion beyond the critical point, the oxidation of starch radicals can be important, there must exist a competition between ceric ion and monomer for the starch radicals, so that the monomer reacts with the most accessible starch radicals and the ceric ion oxidizes the most internal ones. The lower yields were obtained when the small amount of the ceric ion is used. This certainly indicates that mutual termination of growing graft radical chains prevails over the termination due to metal ion.

At the critical point, the highest percentage grafting indicates the ability and extent of the backbone polymer to reduce Ce (IV) to Ce (III) ions. The substraction of hydrogen from starch to form radicals occurs in a suitable extent. The low percentage homopolymer refers to the fact that the formation of monomer radicals is not competitive.

Grafting parameters (%)

Amount of Ce (IV) (g)

$\cdot$ G $+$ G_T $*$ GE $\square$ C_t $\times$ C_g $\diamond$ C_h $\triangle$ C_s
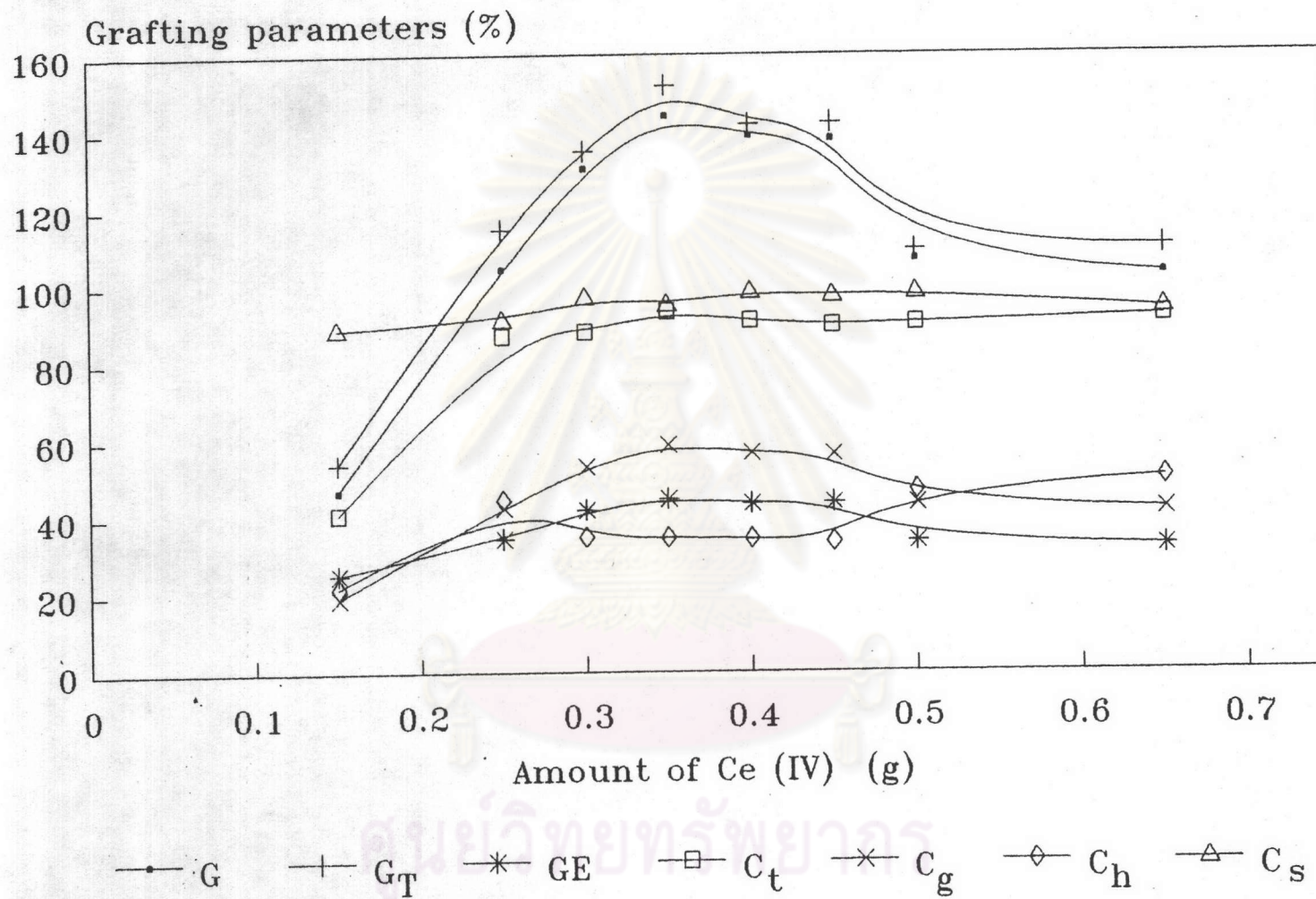
Figure 4.3 Effect of initiator amount on grafting parameters

The decrease observed in percentage grafting and efficiency when large amount of the ceric ion was used, indicates that homopolymerization can compete graft copolymerization. It has been reported that a large proportion of the ceric ion used in the initiation of graft copolymerization remains in the continuous aqueous phase (64) and could initiate homopolymerization of the solubilized monomer. Increase the amount of the ceric ion beyond the critial value results in an increase of homopolymerization more than that of graft copolymerization, as can be realized by comparing the changes of percentage grafting and that of homopolymer. In addition, the large amount of the ceric ion also causes the rapid termination. The inhibitory action of oxygen might be the cause of decrease in grafting yield (60).

The results obtained by varying the amount of Ce (IV) are shown in Figure 4.3. The behavior of the results is similar to that of other results obtained from different systems such as graft copolymerizations of acrylonitrile onto starch (50), methyl methacrylate onto jute fiber (58) and onto wool (61), vinylacetate-methylacrylate mixture onto cellulose (62), and acrylonitrile onto jute fibers (63). The figure clearly shows that there exists a critical amount of ceric ion up to which both the percentage grafting and efficiency increasing and beyond this amount both decreasing.

4.2.4 Effect of variation of monomer

At too large amount of monomer beyond the critical point (Table 3.10), the decrease of grafted products is believed to be caused by the formation of a rubber-like lump. Since at high concentration of monomer the grafting reaction occurs very quickly, thus the fast growing side chains may bind themselves together and suddenly the termination reaches its stage.

Figure 4.4 shows the percentage grafting as a function of the amount of monomer. When the amount of monomer is increased up to the critical point the grafted products depend on the amount of monomer used. This indicates that increase of monomer strongly affects the propagation step of Equation 2.14. The formation of monomer radicals may be increased due to increase of monomer concentration, however, the contact of starch radicals and monomer becomes more important.
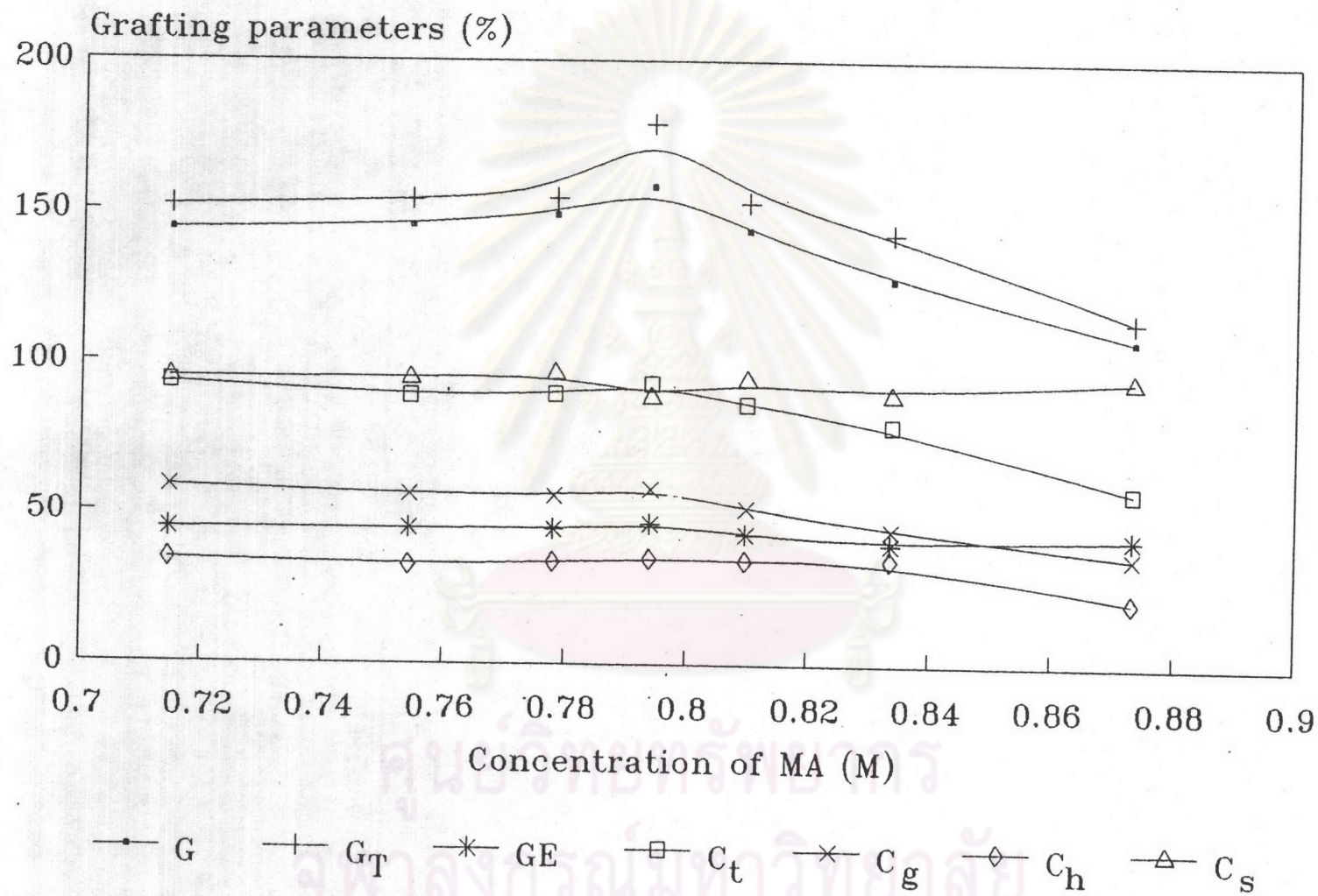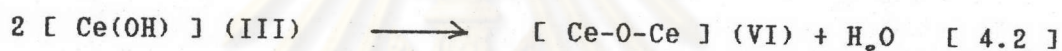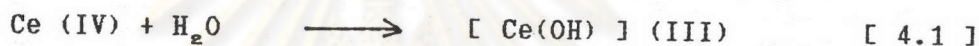
Figure 4.4 Grafting parameters as functions of monomer concentrations

4.2.5 Effect of the amount of nitric acid

From Table 3.12, it is observed that   if the amount
of   nitric   acid   was   increased   beyond the optimum value, the
grafting yield was found to be decreased. The decrease in graft
yield can be explained by the postulated behavior of the ceric
ion which exists in water in different oxidation stages as Ce(IV),
[Ce(OH)] (III), and [Ce-O-Ce] (VI) as the following manner:

$$Ce \ (IV) + H_2O \longrightarrow \qquad [\ Ce(OH) \ ] \ (III) \qquad [\ 4.1 \ ]$$

$$2 \ [\ Ce(OH) \ ] \ (III) \longrightarrow \qquad [\ Ce-O-Ce \ ] \ (VI) + H_2O \quad [\ 4.2 \ ]$$

With the increase of the amount of nitric acid beyond the
critical value, the equilibrium was found to shift towards the
formation of colloquial Ce (IV) and $[Ce(OH)_3]$ (III) ions. These
species at higher amount adversely affect grafting parameters.

The behavior found when the amount of nitric acid is
varied is similar to the general dependence reported by other
authors (61, 63).   In the Figure 4.5, there exists a critical
amount of nitric acid (mole) which affords maximum grafting.
It has been observed that changes in the concentration of nitric
acid affect the rate of oxidation of ethanol (65) and butane-
diol (66, 67) by the ceric ion via the formation of an interme-
diate complex between the ceric ion and those compounds. At low
concentration of nitric acid, the increase of nitric acid
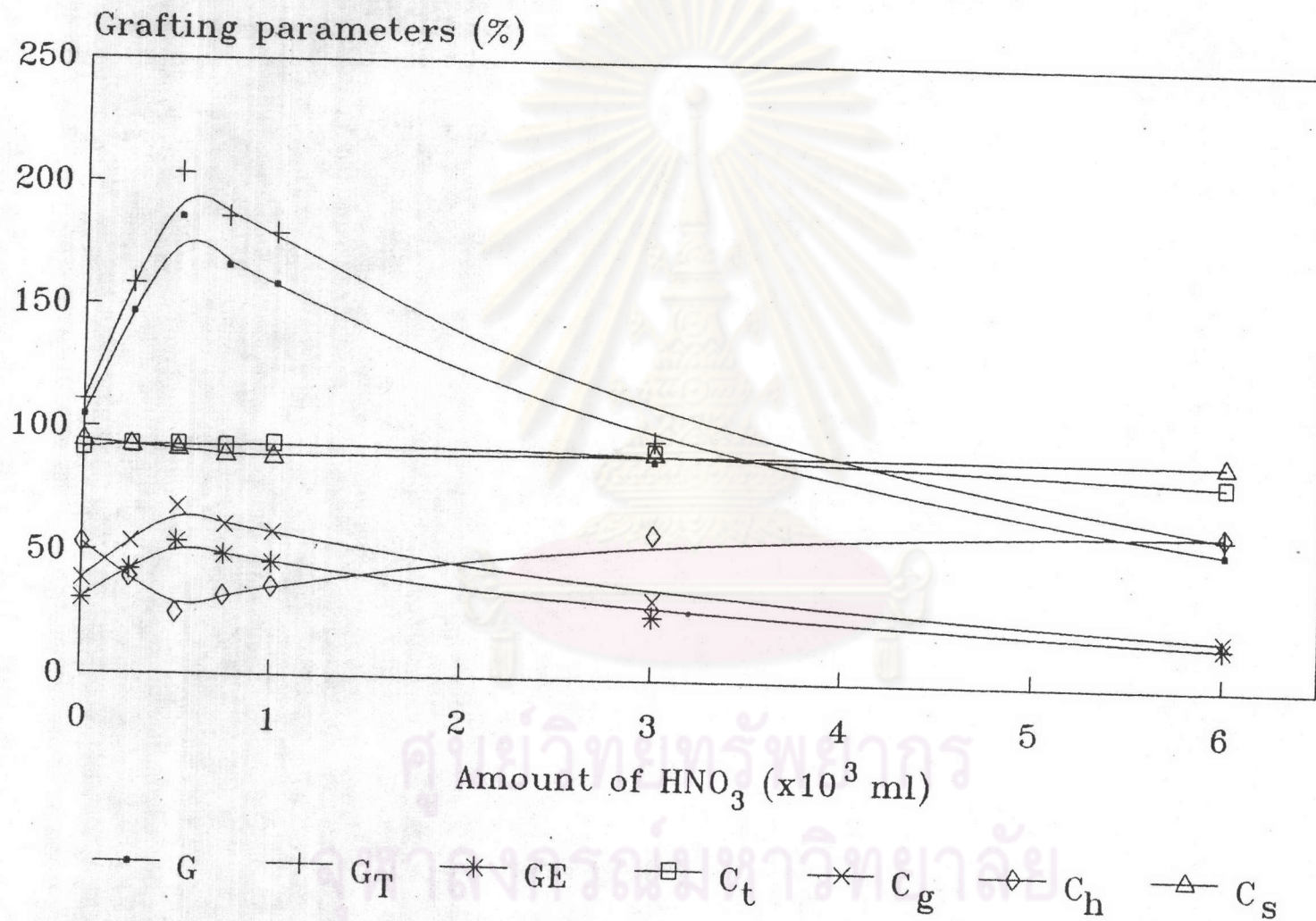concentration produced higher equilibrium constant of the complex

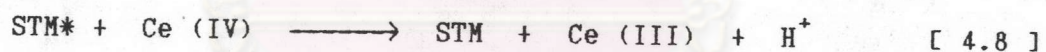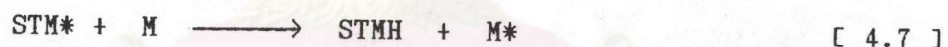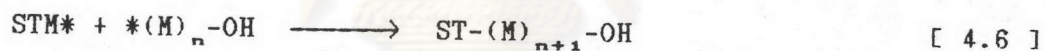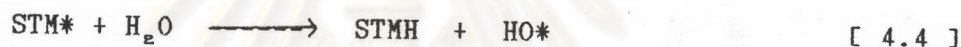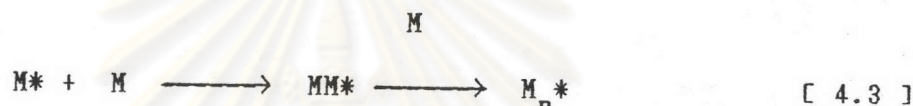Figure 4.5 Effect of amount of nitric acid on grafting parameters

formation. It can be implied that the increase of nitric acid up to the value which gives maximum grafting yield and the according parameters may increase the formation of Ce(IV)-starch complex and thus the following dissociation of the complex to give starch radicals is believed to be increased too. By this reason, the rate of grafting initiation and of propagation are certainly predominant over the rate of termination and of starch oxidation.

4.2.6 <u>Effect of variation of reaction temperature</u>

Along with the further increase of temperature beyond
45 ° C (Table 3.14), the percentage graftng yield was
decresed.   This   indicates   that   at   higher   temperature,
homopolymer formation becomes predominant by the process
represented by Equation 4.5 in the postulated mechanism reported
by Misra, et al. (68):

$$M* + M \longrightarrow MM* \xrightarrow{M} M_n*$$ [4.3]

$$STM* + H_2O \longrightarrow STMH + HO*$$ [4.4]

$$HO* + M \longrightarrow HO-M* \xrightarrow{M} HO-(M)_n*$$ [4.5]

$$STM* + *(M)_n-OH \longrightarrow ST-(M)_{n+1}-OH$$ [4.6]

$$STM* + M \longrightarrow STMH + M*$$ [4.7]

$$STM* + Ce (IV) \longrightarrow STM + Ce (III) + H^+$$ [4.8]

At higher temperature, the termination of grafting chain growth
by the process 4.8 is responsible for the decrease of percentage
graft parameters.

The Figure 4.6 shows the percentage grafting and
efficiency as the funtions of temperature.   The increase of
temperature up to 45 ° C makes the percentage graft on increase.
In a complex system like this, several reactions might be taking
place simultaneously, such as (i) solution of the monomer in the
reaction medium and its diffusion from the solution phase to the
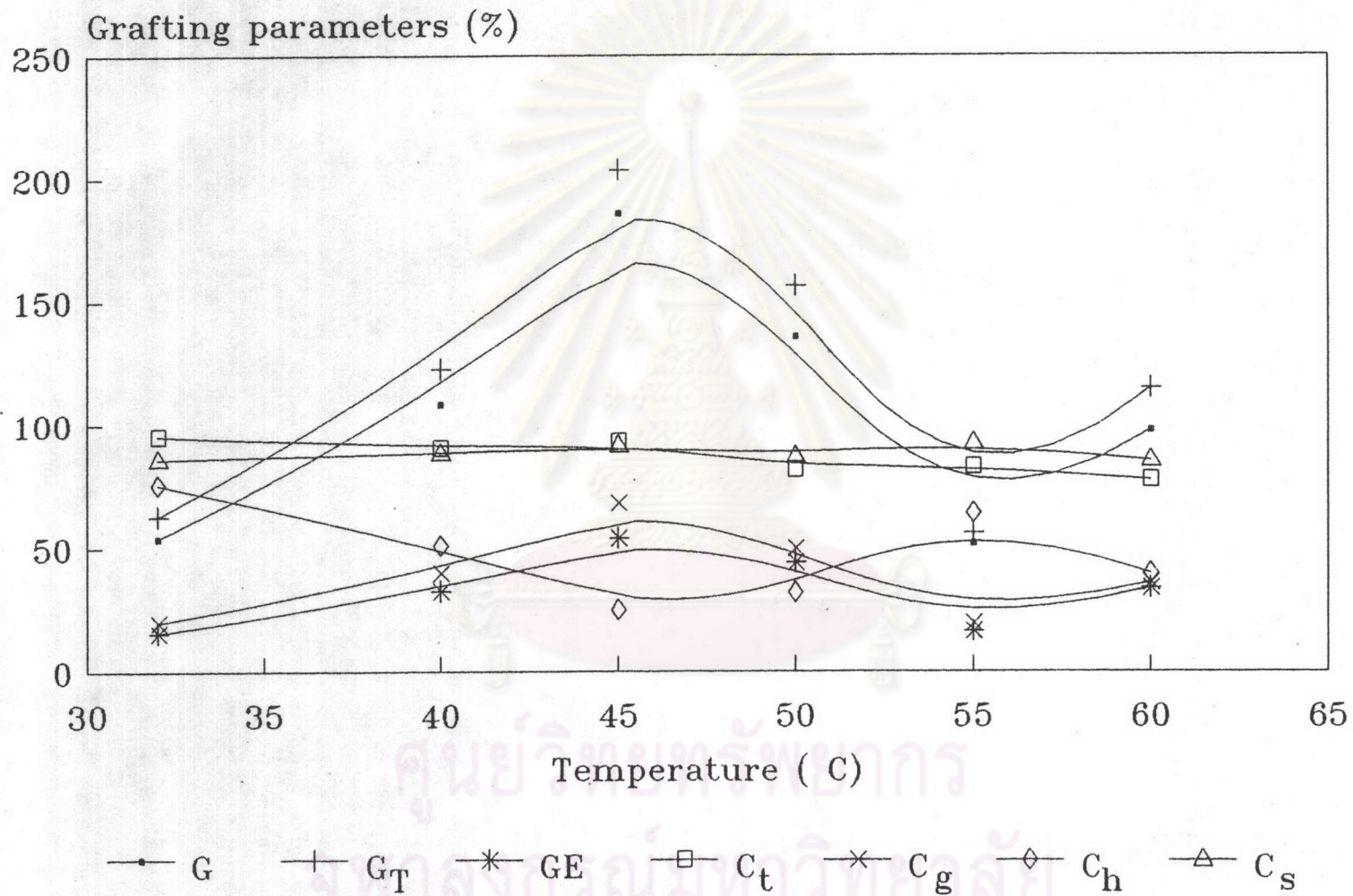
Figure 4.6 Effect of temperature on grafting parameters

starch phase, (ii) adsorption of the monomer onto the starch and its complexation with starch molecules to enhance availability and reactivity of the monomer, (iii) formation and propagation of graft on starch, and (IV) enhancement of the activation of monomer. The net effect of all these factors is higher grafting with increase of temperature (69, 70).

The percentage grafting was increased again at 60 $^{\circ}$C. This can be attributed to the favorable influence of temperature on starch gelatinization and increase of starch amorphous region. The partial gelatinized starch is believed to be obtained at this temperature. So the diffusion of the ceric ion to starch chains takes place easily and the active sites of starch are increased in the system under this situation.

4.2.7 Graft copolymerization of methylacrylate onto different starches

The starches from different sources can undergo graft copolymerization with different efficiencies. The starches which become glutinous rapidly and more sticky seem to undergo the reaction with high efficiency. This may be seen in the cases of cassava and glutinous rice starch. The starches from tubers, eg., cassava starch is very effective.

4.3 Preliminary biodegradation study of polymer films

The results represented in Tables 3.17-3.21 show that the films of PCL, Starch-g-PMA and their polymer blends can be degraded by fungi. This indicated that the ester bonds on linear aliphatic polyesters of PCL and the ether linkages on polysaccharide skeletons of Starch-g-PMA must be cleavaged by hydrolytic enzyme released from fungi cells.

The evidences of more crowded covering fungi spore on the PCL and Starch-g-PMA films indicate that PCL and Starch-g-PMA are potentially biodegradable. The observed growth of fungi on them indicates that they can be degraded easier than their polymer blends. It can be explained by the following reasons:

(1) The biodegradation of polymer films occurs first at the surface and then move forward into the inner mass.

(2) The PCL film's surface is composed of an unique biodegradable constituent which is the same as the composition of the mass.

(3) Starch-g-PMA is composed of two constituents, starch and PMA, which have different properties so the films' surface is microscopic heterogeneous. However, the biodegradable grafted starches which support the growth of fungi disperse orderly through out the surface and the inner mass.

The polymer blends of PVAc with PCL or Starch-g-PMA have more potential to be degraded than that of PVC as they were found to support more growth of fungi. This may be resulted from the difference in microbial resistance of PVAc and PVC. It has been reported that PVC has very high resistance to microorganisms but the resistance of PVAc is moderate (71).

The irregular relationship between weight ratio of PCL in polymer blends and the percentage molecular weight loss was obtained in this research as shown in Table 3.22. The result may be affected by the disorderly distribution of constituents on film's surface. The film's surface of polymer blends is covered by both biodegradable and bioinert fractions. The area covered by PCL may not be related to the weight ratio of used PCL due the less efficiency of blending procedure. The distribution of the compositions in the inner mass of the films is also disorderly as that of the surface. The orderness of constituent distribution may be controlled by the more efficient blending processes and equipments so that the biodegradation rate can be controlled.