CHAPTER IV

RESULTS AND DISCUSSION

Based on the previous work of Fanta et.al (29), an addition rate of precipitation in methanol (0.0167 cm^3/s) with constant and thorough mixing was used in the preparation. It is found that, due to the ensured complete absorption of methanol, the graft copolymer was precipitated individually with micron-sized gel/minute particle size, which gave a smooth, free flowing gel dispersion in water. It is presumed at this stage that, a thickener of cassava starch grafted with poly(acrylic acid) was obtained.

Results and Discussion

4.1   Characteristic of the Hydrolyzed Starch-g-Poly(acrylic acid) Copolymer by Infrared Spectroscopy

Theoretically, graft copolymerization of vinyl monomer onto starch is always accompanied by a homopolymer formation. The grafting functional groups of the products were characterized by an FT-IR technique to detect the presence of functional groups of the grafted product after saponification and methanol addition. The homopolymer of sodium acrylate was soluble in methanol from which it was separated.

Infrared spectra of cassava starch and the hydrolyzed starch-g-poly(acrylic acid) copolymer in the form of KBr pellets are reported in Figures 4.1-4.2, respectively.
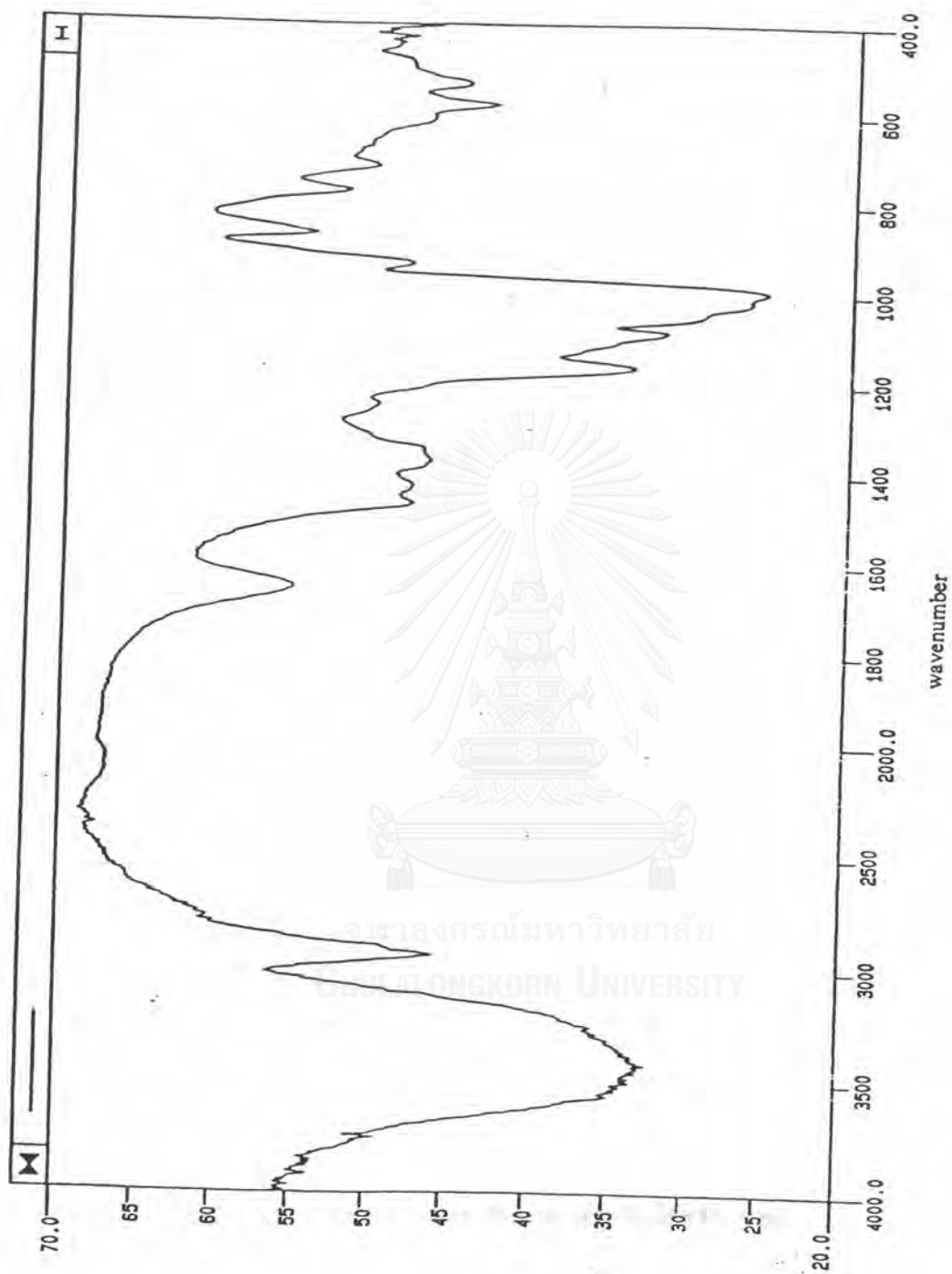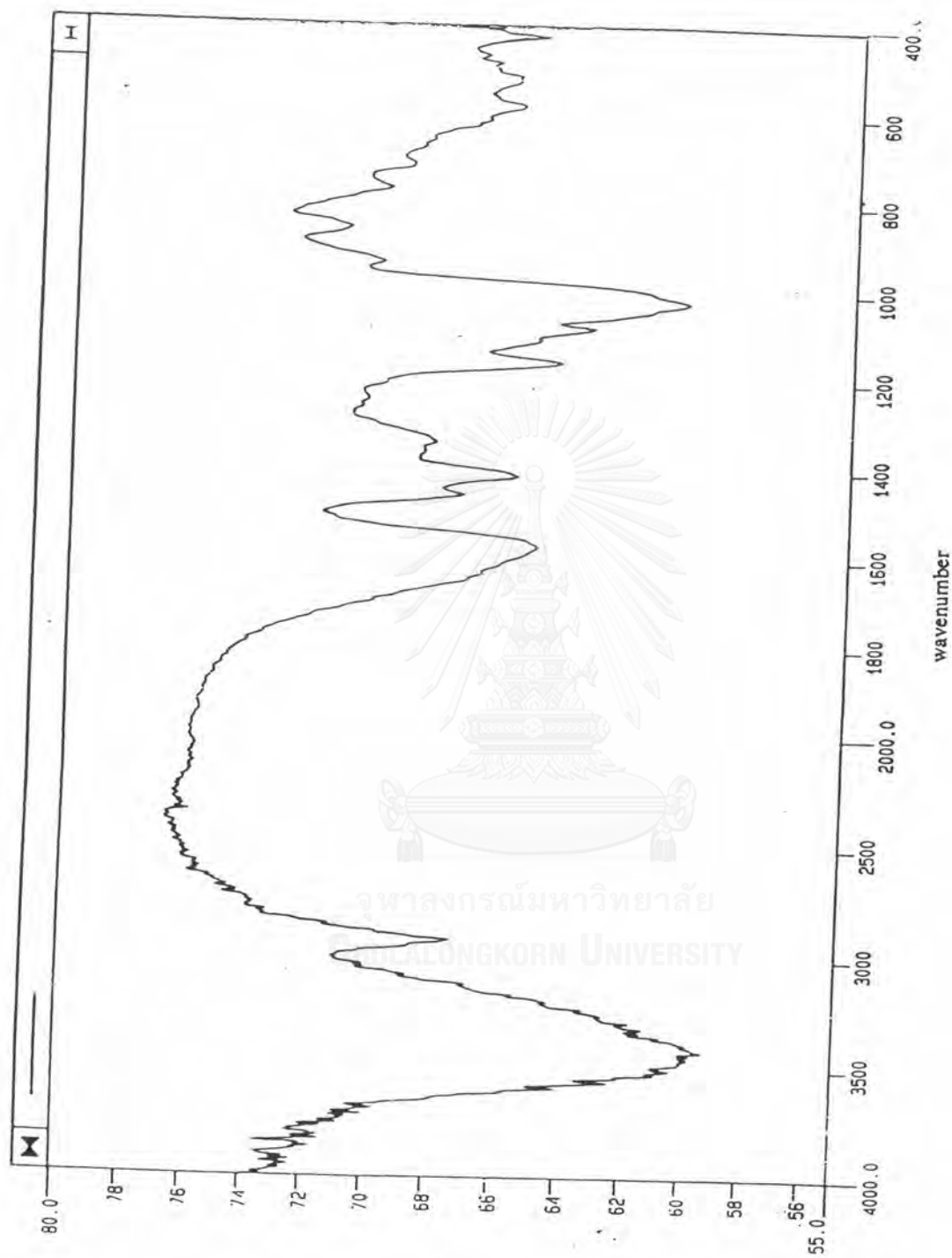
Figure 4.1 Infrared spectrum of dried cassava starch

Figure 4.2 Infrared spectrum of hydrolyzed starch-*g*-poly(acrylic acid)

The FT-IR Spectrum of cassava starch in Figure 4.1 shows the following important peaks in Table 4.1

TABLE 4.1

The Infrared Absorption of Functional Groups in Cassava Starch

Wavenumber, cm^{-1}	Assignment
3,500-2,500	O-H stretching
2,931	C-H stretching of CH_2
1,462	C-H scissors bending of CH_2
1,159	C-O-C stretching
1,084	C-O stretching
710	C-H rocking of CH_2

The FT-IR spectrum of cassava starch in Figure 4.1 gives absorption bands at 3,500 and 1,000-1,200 cm^{-1}, the characteristics of amylose containing in the starch. After redox initiation of the acrylic acid onto the starch, one can observe the distinguished absorption peaks in the FT-IR spectrum of the hydrolyzed starch-g-poly(acrylic acid) copolymer in Figure 4.2, which indicate the occurrence of graft copolymerization of acrylic acid onto starch in which the absorption peaks of the C=O stretching occur at 1,650 cm^{-1}, and the C=O and C-O asymmetry and symmetry stretching of carboxylate anions occur at 1,575 and 1,415 cm^{-1}, respectively (48). The latter two peaks show that poly(acrylic acid) grafts are converted into their inorganic salt (sodium polyacrylate), while the starch-g-poly(acrylic acid) was saponified to the sodium salt of the copolymer. The absorption peak of cassava starch still

exists. It indicates that acrylic acid was probably grafted on the starch backbone.

The FT-IR spectrum of the hydrolyzed starch-*g*-poly(acrylic acid) copolymer in Figure 4.2 shows the following peaks in Table 4.2

TABLE 4.2

The Infrared Absorption of Functional Groups

in Saponified Starch-*g*-Poly(acrylic acid)

Wavenumber, cm^{-1}	Assignment
3,500-2,800	O-H stretching
2,922	C-H stretching of CH$_2$
1,650	C=O stretching
1,575	C=O and C-O asymmetrical stretching of the carboxylate anion
1,450	C-H scissors bending
1,415	C=O and C-O symmetrical stretching of the carboxylate anion
1,157	C-O-C stretching

4.2. Characteristic of the Hydrolyzed Starch-*g*-poly(acrylic acid) Copolymer by Nuclear Magnetic Resonance Spectroscopy

^{13}C-NMR finds increasing and intensive use in the characterization of polymers. Brame and Kahn (49) stressed that ^{13}C-NMR analysis could

provide detailed information on the microstructure and copolymer. In this techniques, D_2O was used as solvent. Comparisons of ^{13}C-NMR chemical shifts of the copolymer with the ^{13}C-NMR spectrum of acrylic acid monomer, cassava starch, and hydrolyzed starch-*g*-poly(acrylic acid) copolymer are presented in Table 4.3 and Figures 4.3-4.5, respectively.

Figure 4.3 is the ^{13}C-NMR spectrum of acrylic acid monomer, the peaks appearing at the low field region (100-190 ppm) may possibly be assigned as follows: (i) at 129.99 ppm is the =CH- group; (ii) at 134.89 ppm is the =CH_2 group; and (iii) at 172.15 ppm is the COOH group. The calculation of ^{13}C-NMR chemical shifts (δ in ppm relative to TMS) of sp^2-hybridized carbon in an unsaturated vinyl compound (50) has a formula as shown in eq 4.1.

$$\delta_{ci} = 123.3 + Z_i \qquad (4.1)$$

(i = 1,2,3,...n)

Acrylic acid has the structure of CH_2=CH-COOH

(2)   (1)

$$\begin{aligned}
\delta_{c1} &= 123.3 + Z_1 \text{ (substituent group =CH-)} \\
&= 123.3 + 5.0 \\
&= 128.3 \text{ ppm} \\
\delta_{c2} &= 123.3 + Z_2 \text{ (substituent group =}CH_2) \\
&= 123.3 + 9.8 \\
&= 133.1 \text{ ppm}
\end{aligned}$$

^{13}C-NMR chemical shift for the $-\overset{\overset{O}{\|}}{C}-$ in the carboxylic compound is 171.7 ppm. As shown in Figure 4.3, ^{13}C-NMR chemical shifts from the
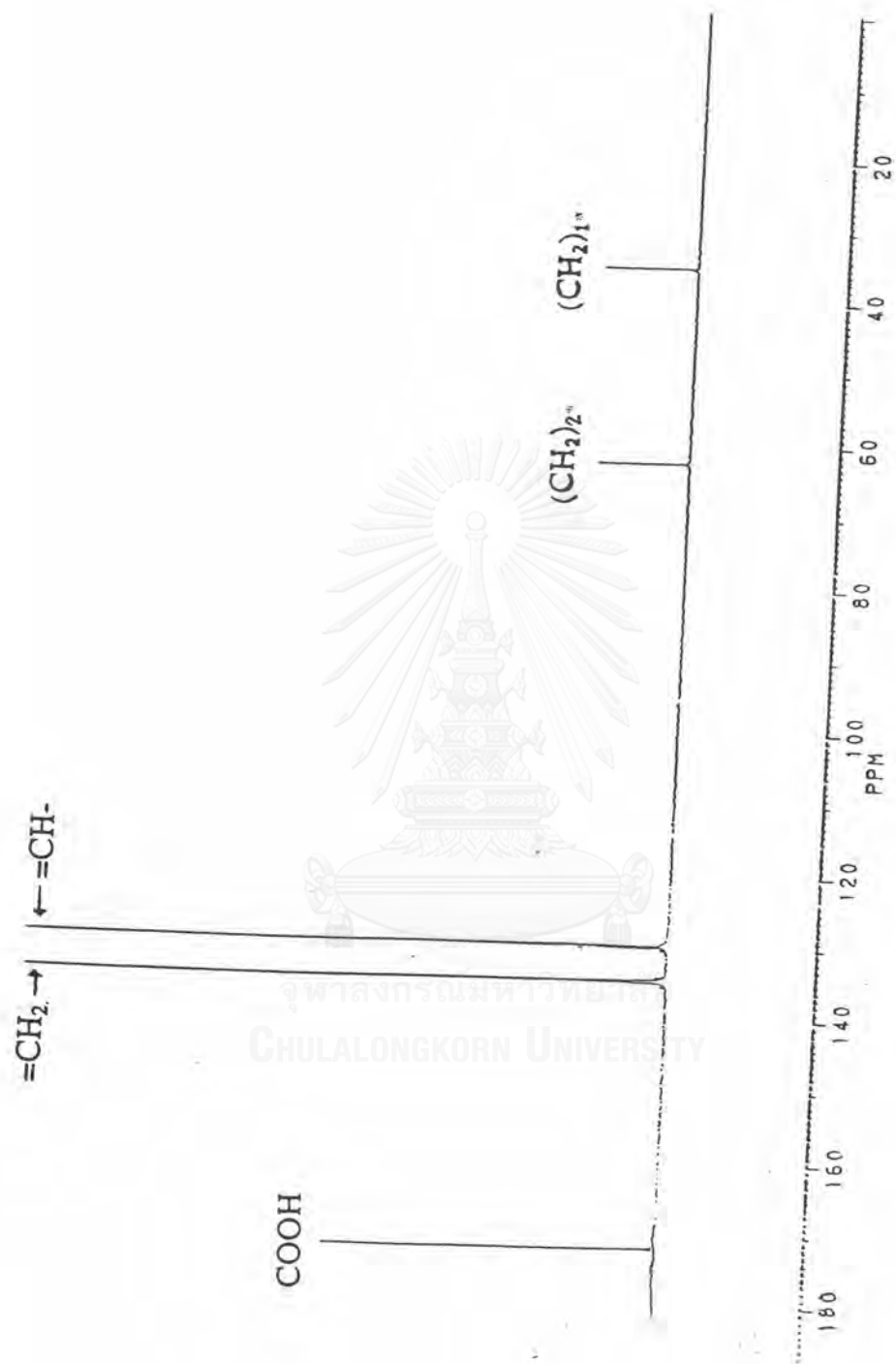
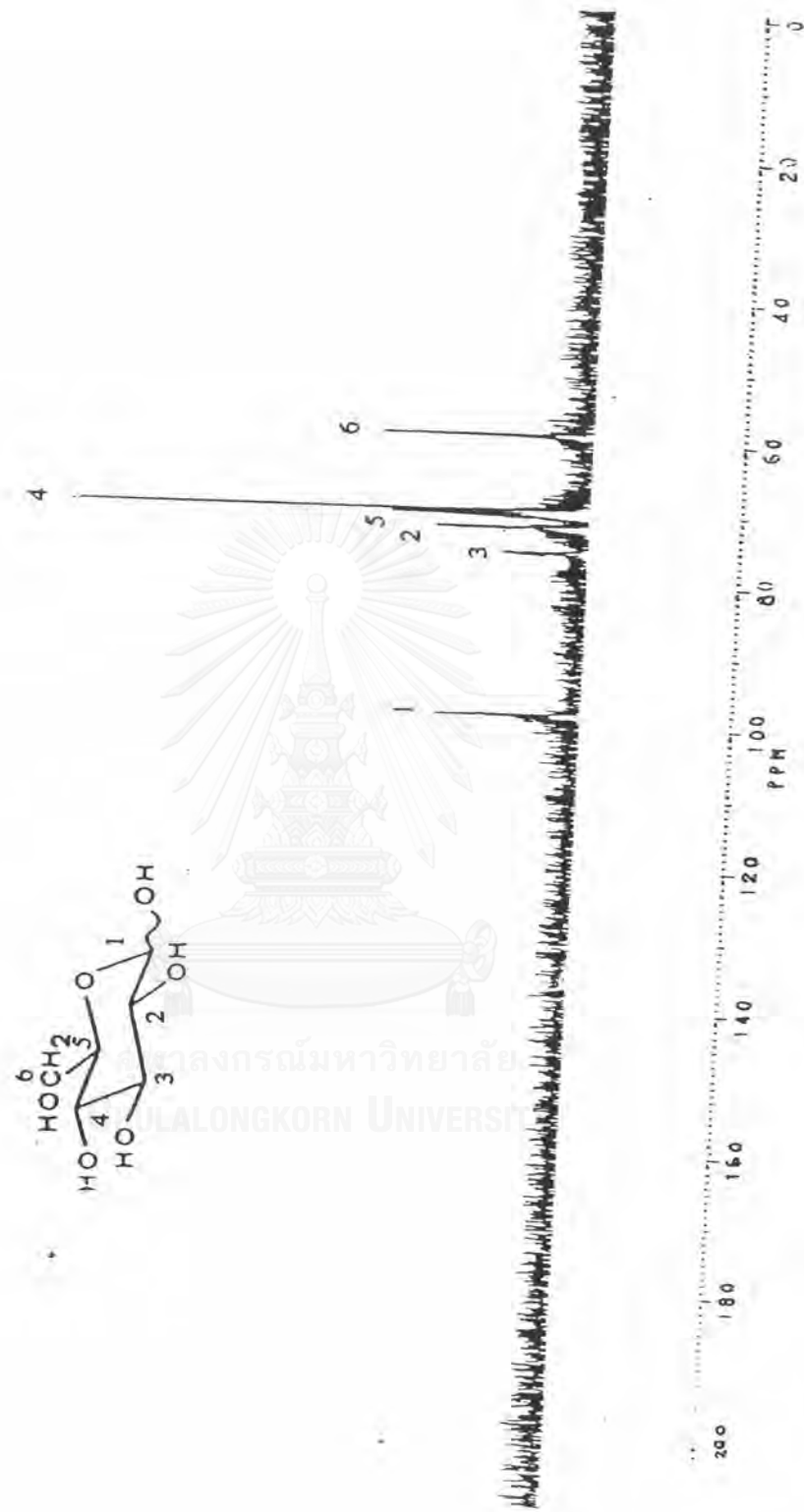Figure 4.3 ^{13}C- NMR spectrum of acrylic acid monomer

Figure 4.4 ^{13}C-NMR spectrum of α-D-glucopyranosyl units containing in the dried cassava starch
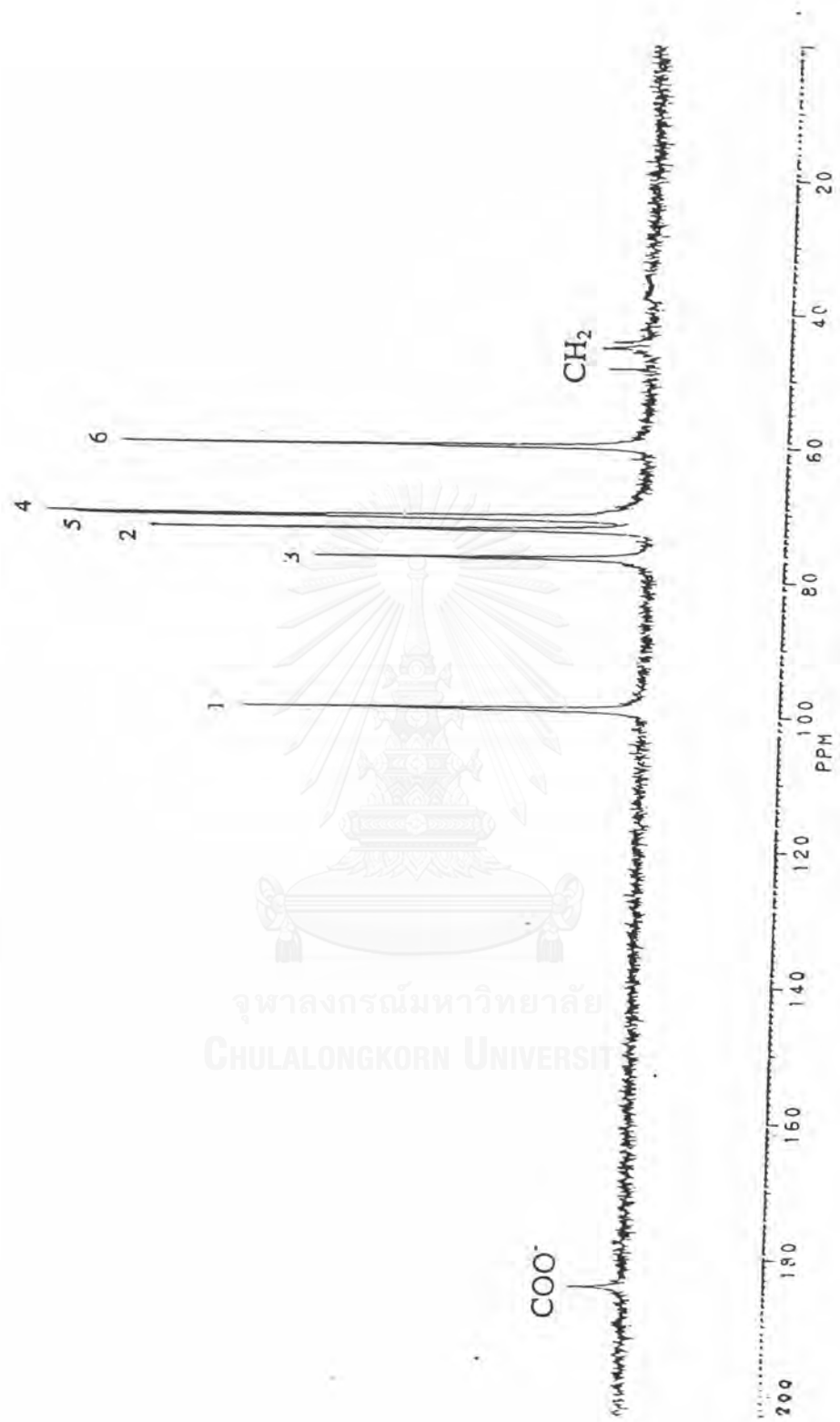
Figure 4.5 ^{13}C-NMR spectrum of hydrolyzed starch-*g*-poly(acrylic acid)

Table 4.3   The ^{13}C-NMR Chemical Shifts of Functional Groups in Acrylic Acid Monomer, Cassava Starch, Copolymer after grafting

Acrylic Acid Monomer		Cassava Starch		Graft Copolymer after Grafting	
chemical shift (ppm)	assignment	chemical shift (ppm)	assignment	chemical shift (ppm)	assignment
172.75	COOH	98.70	C_1	184.32	COO$^-$
134.89	=CH$_2$	72.67	C_2	99.21	C_1
129.99	=CH-	75.37	C_3	72.83	C_2
62.74	(CH$_2$)$_2$*	70.34	C_4	76.94	C_3
35.83	(CH$_2$)$_1$*	70.46	C_5	70.88	C_4
		59.37	C_6	71.75	C_5
				60.21	C_6
				45-46	Multiple peaks of CH$_2$
				50.27	Single peak of CH$_2$

spectrum were nearly similar to that of the calculated data. The peaks appearing in the high field region are assigned to the -CH_2- group of acrylic acid. The peaks at 62.74 and 35.83 ppm were assigned to the $(CH_2)_{2*}$ and $(CH_2)_{1*}$ from a dimerization of acrylic acid having the following structure:

$$HOOC-CH_2-CH_2-CH_2-CH_2-COOH.$$

2*   1*
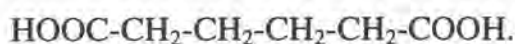
The ^{13}C-NMR spectrum of cassava starch was shown in Figure 4.4. The ^{13}C-NMR chemical shifts at 98.70, 72.67, 75.37, 70.34, 70.46, and 59.37 ppm, were assigned to the carbon positions at C_1, C_2, C_3, C_4, C_5 and C_6 of cassava starch.

^{13}C-NMR spectrum in Figure 4.5 is starch-g-poly(acrylic acid). The peak at 184.32 ppm is probably related to the carboxylate anion, COO^-, from poly(acrylic acid) grafts that are converted into their inorganic salt of sodium polyacrylate when the starch-g-poly(acrylic acid) was saponified.

It is inevitable from the spectra, that the peaks of the =CH_2 and =CH- in acrylic acid monomer were disappeared. It can be explain as follow. During the polymerization reaction, the double bond in the monomer was opened by the reaction. According to the influence of the polymerization, the peaks at 45-46 and 50.27 ppm were assigned to the -CH_2- group in polyacrylate chain (50). As a result, the grafted polyacrylate side chains had different repeating units of the monomer, then the chemical shifts of the -CH_2- were affected within the range mentioned above. The chemical shifts at 99.21, 72.83, 76.94, 70.88, 71.15, and 60.21 ppm were assigned to the carbon positions of C_1, C_2, C_3, C_4, C_5 and C_6 of cassava starch. This confirmes that acrylic acid has been grafted to the backbone of the cassava starch, the main grafting substrate. Since a new signal appeared adjacent to C_6 of AGU (59.37

compared to 60.21 ppm of the literature value), which was suspected to be the produced as a result of the reaction of starch with acrylic acid at this position.

4.3. Water Absorption of the Saponified Starch-g-Poly(acrylic acid) Copolymer

The mechanism for the grafting polymerization of acrylic acid monomer (M) onto the cassava starch via hydrogen peroxide and L(+)-ascorbic acid as a redox system is shown below:

a) Redox System (47)

This method used a reducing agent of L(+)-ascorbic acid (vitamin C) as an accelerator for organic/inorganic peroxide (this research used hydrogen peroxide). In an aqueous system, ascorbic acid is reversibly oxidized to dehydro-ascorbic acid (DHA) as shown in eq 4.2. .
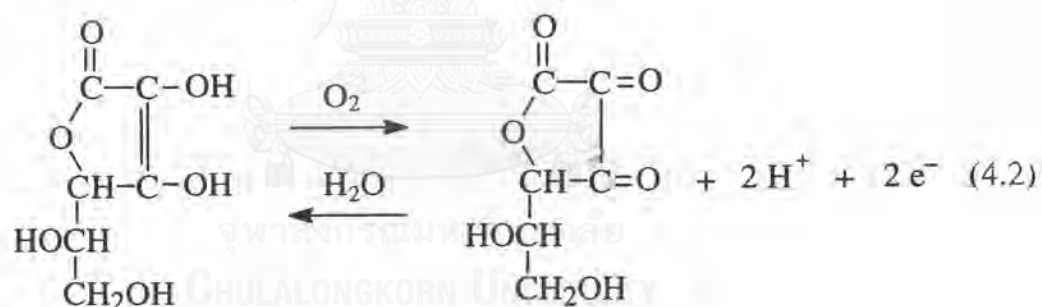
L(+)-ascorbic acid   Dehydro-ascorbic acid

Appearently this redox reaction proceeds by a two successive one-electron transfer reaction, which suggests that its chemical property is responsible for its accelerative action with hydrogen peroxides. The free radicals (R$^•$) are created by this method. A possible proton-assisted one-electron transfer mechanism for an oxidation reaction is shown in eq 4.3.

$$\text{(structure)} + \text{(H}_2\text{O}_2) \rightarrow \left[\text{(structure)} + \cdot\overset{\oplus}{\text{O}} \text{ H}^{\oplus} \right] \rightarrow \text{(structure)} + \text{HO}^{\cdot} + \text{H}_2\text{O} \qquad (4.3)$$
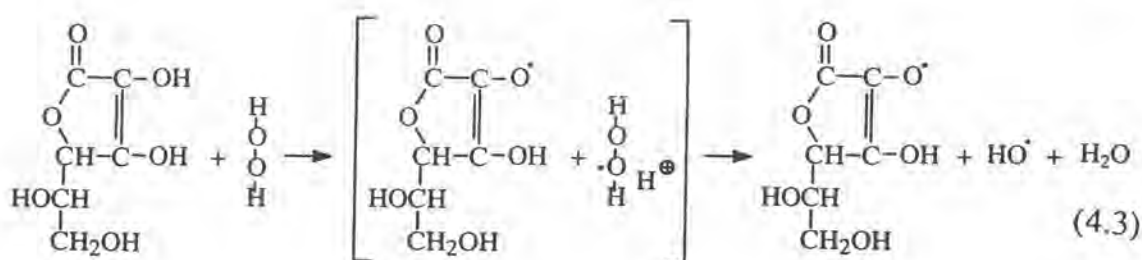
Increasing the reaction temperature is expected to cause a faster rate of hydrogen peroxide decomposition to water and oxygen gas. The oxygen molecules can then oxidize L(+)-ascorbic acid to dehydroascorbic acid, a non-reactive species for the graft polymerization as shown in eq 4.2 (47).
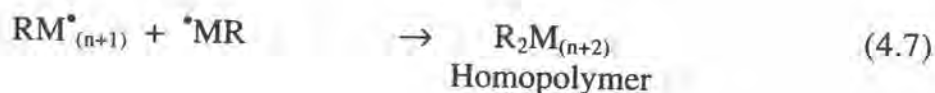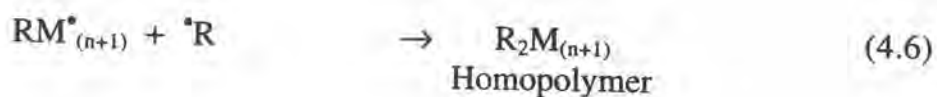
The number of free radicals is responsible for the relative amounts of homopolymer and copolymer. The homopolymerization and graft polymerization take place simultaneously and competitively.

b) <u>Homopolymerization</u>

$$R^{\cdot} + M \text{ (monomer)} \rightarrow RM^{\cdot} \qquad (4.4)$$

$$RM^{\cdot} + nM \rightarrow RM^{\cdot}_{(n+1)} \qquad (4.5)$$

$$RM^{\cdot}_{(n+1)} + {}^{\cdot}R \rightarrow R_2M_{(n+1)} \qquad (4.6)$$
$$\text{Homopolymer}$$

$$RM^{\cdot}_{(n+1)} + {}^{\cdot}MR \rightarrow R_2M_{(n+2)} \qquad (4.7)$$
$$\text{Homopolymer}$$

c) <u>Graft polymerization</u>

$$R^{\cdot} + \text{S-H (starch)} \rightarrow S^{\cdot} + \text{R-H} \qquad (4.8)$$

$$S^\bullet + nM \qquad \rightarrow \qquad SM_n{}^\bullet \qquad\qquad (4.9)$$

$$SM_{(n+1)}{}^\bullet + RM^\bullet \qquad \rightarrow \qquad SRM_{(n+2)} \qquad\qquad (4.10)$$
$$\text{graft copolymer}$$

$$SM_n{}^\bullet + R^\bullet \qquad \rightarrow \qquad SRM_n \qquad\qquad (4.11)$$
$$\text{graft copolymer}$$

$$S^\bullet + RM^\bullet{}_{(n+1)} \qquad \rightarrow \qquad SRM_{(n+1)} \qquad\qquad (4.12)$$
$$\text{graft copolymer}$$

d) Radical termination

$$R^\bullet + R^\bullet \qquad \rightarrow \qquad RR \qquad\qquad (4.13)$$
$$\text{recombination}$$
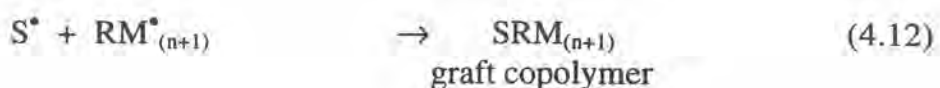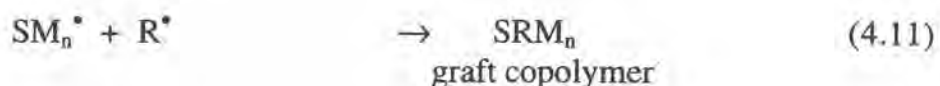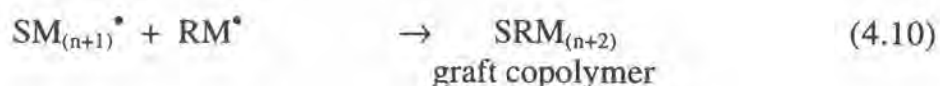
$$R^\bullet + RM^\bullet \qquad \rightarrow \qquad RMR \qquad\qquad (4.14)$$
$$\text{primary termination}$$
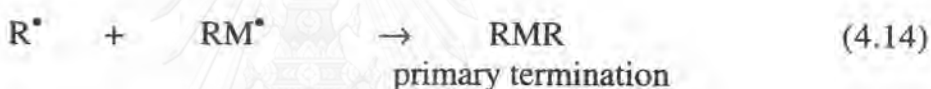
4.3.1 Effect of Acrylic Acid concentration

The effect of AA concentrations on percent graft copolymer and the water absorption of the saponified starch-*g*-PAA copolymer in deionized distilled water is tabulated in Table 4.4 and shown in Figures 4.6-4.7, respectively.

The experiment data show that the percentage graft copolymer decreases while the amount of AA increases. This result can be perhaps, explained in the term of homopolymer content. The excess monomer present in the reaction medium participates mainly in the homopolymerization reaction than does in the copolymerization which can be due to the following reasons: increasing acrylic acid concentrations could be associated with greater availability of the monomer molecules, the decreasing tendency of grafting

TABLE 4.4

Effect of the Acrylic Acid Concentration on the

Saponified Starch-*g*-Poly(acrylic acid) Copolymers.

AA (M)[a]	%homo-polymer	%graft copolymer	Water absorption in deionized distilled water (g/g)
1.70	4.1	95.9	5
2.06	6.7	93.3	28
2.40	9.7	90.3	36
2.73	12.4	87.6	62

[a]Data were obtained under the following condition: starch = 60 g,

$[H_2O_2] = 1.94 \times 10^{-1} M$, ascorbic acid = 0.33%, reaction time = 3 h,

reaction temperature = 35°C

occured when monomer concentrations were higher than 1.70M. Most probable formation of larger amounts of poly(acrylic acid) at higher monomer concentration within the starch would impede diffusions of both monomer and initiator to the starch, thereby lowering the graft copolymerization. It is rather likely that homopolymerization prevails over grafting at higher acrylic acid concentrations, and as a result, short propagation chains can be terminated by the termination reaction between themselves or with a few active sites of the polymer substrate to get a very short graft, a lower graft copolymerization is thus obtained. Indeed, a significant amount of homopolymer formation was observed when higher acrylic acid concentrations were used (51). As a result, the monomer concentrations to effect the water absorption was also found increasing.

Figure 4.6 Effect of acrylic acid concentration on percent graft copolymer

Figure 4.7 Effect of acrylic acid concentration on water absorption of starch-*g*-poly(acrylic acid) copolymer in deionized distilled water
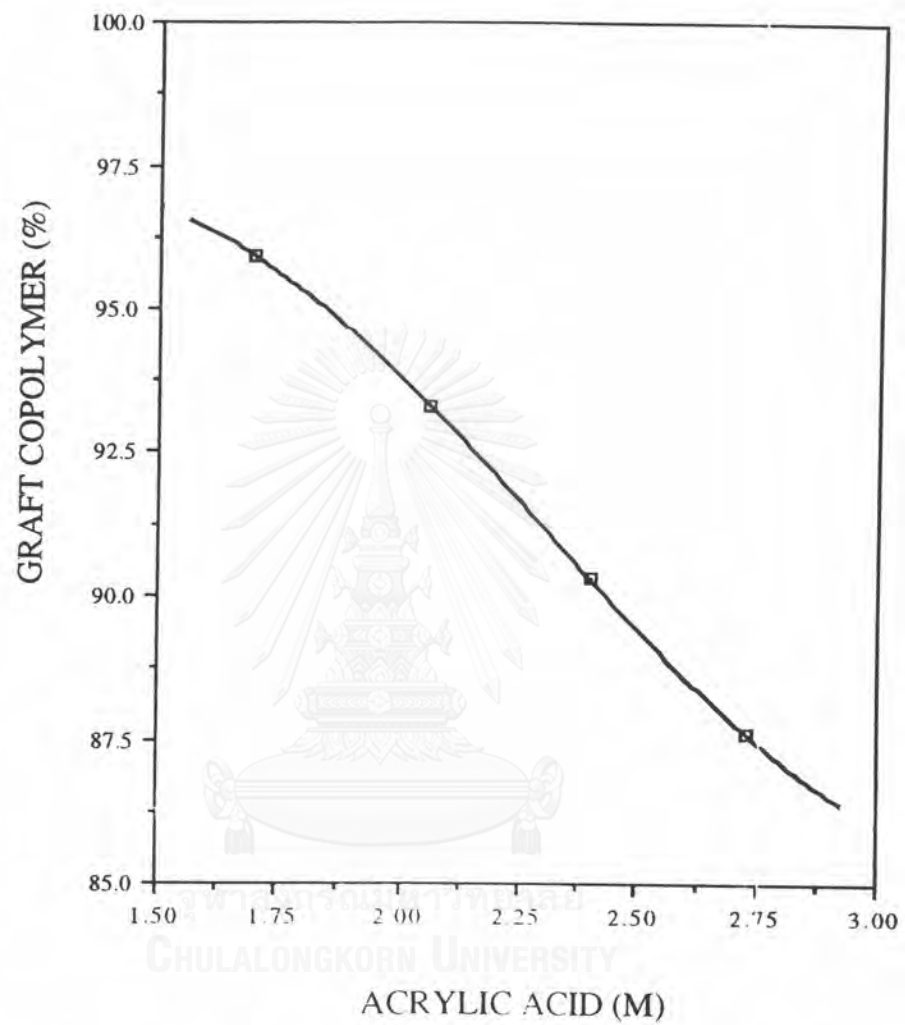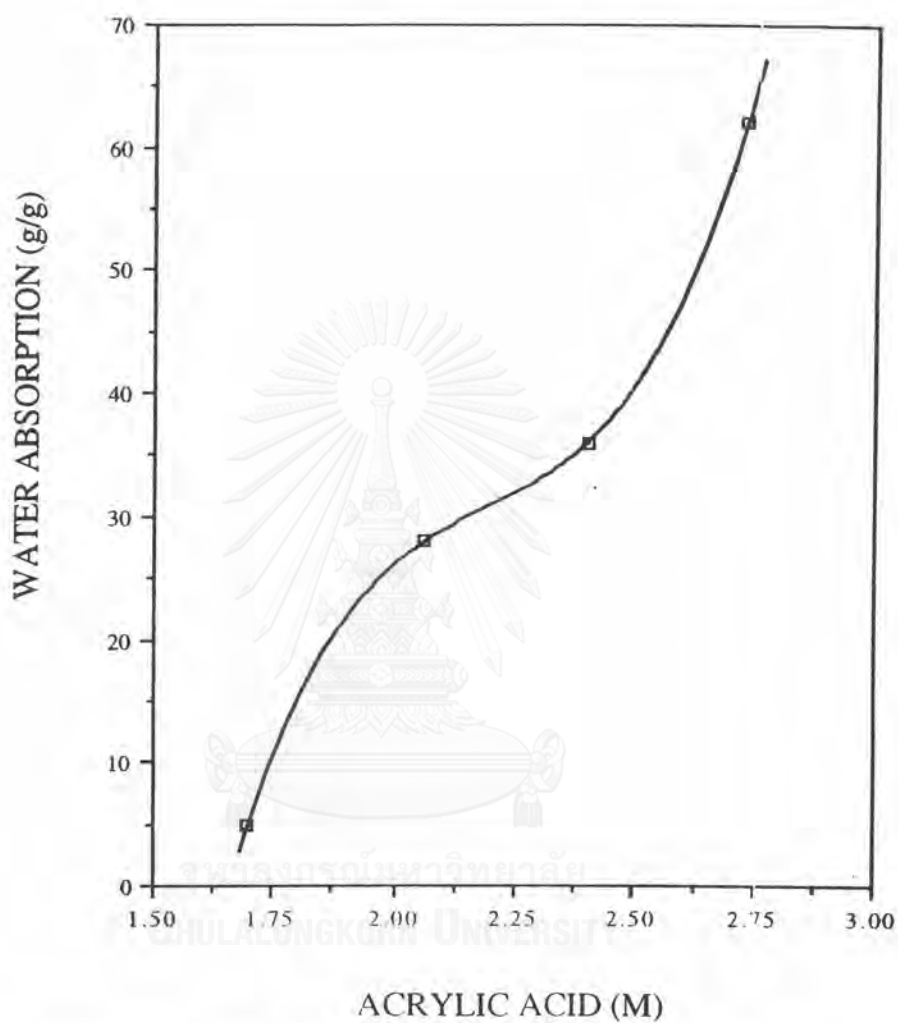
4.3.2 Effect of Hydrogen Peroxide Concentration

The effect of hydrogen peroxide concentrations on percent graft copolymer and the water absorption of the saponified starch-g-PAA copolymer in deionzied distilled water is tabulated in Table 4.5 and shown in Figures 4.8-4.9, respectively.

TABLE 4.5

Effect of the Hydrogen Peroxide Concentration on the

Saponified Starch-g-Poly(acrylic acid) Copolymers

H_2O_2 (M)[a]	%homo- polymer	%graft copolymer	Water absorption in deionized distilled water (g/g)
9.70×10^{-2}	7.0	93.0	5
1.94×10^{-1}	4.1	95.9	5
2.90×10^{-1}	6.5	93.5	26
3.86×10^{-1}	6.8	93.2	38

[a]Data were obtained under the following condition: starch = 60 g, [AA] = 1.70M, ascorbic acid = 0.33%, reaction time = 3 h, reaction temperature = 35°C

The experiment data show that the graft copolymer increases until the hydrogen peroxide concentration increases to 1.94×10^{-1}M. Above this concentration, the increment in graft copolymer is not so striking.

The effect of hydrogen peroxide concentration on the water absorption and graft copolymer could be explained as follows: when an aqueous solution of hydrogen peroxide is heated, it decomposes to produce the hydroxyl radicals. Logically, the amount of radical species will be higher at the
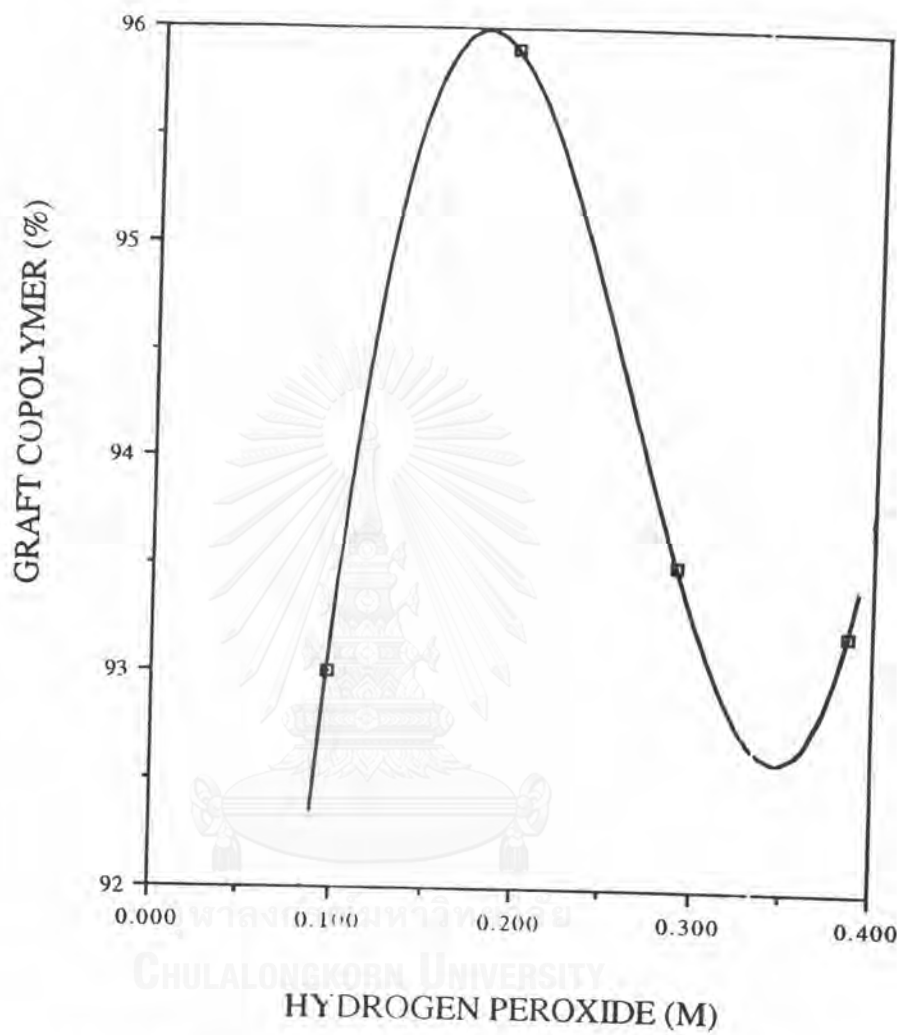
Figure 4.8 Effect of hydrogen peroxide concentration on
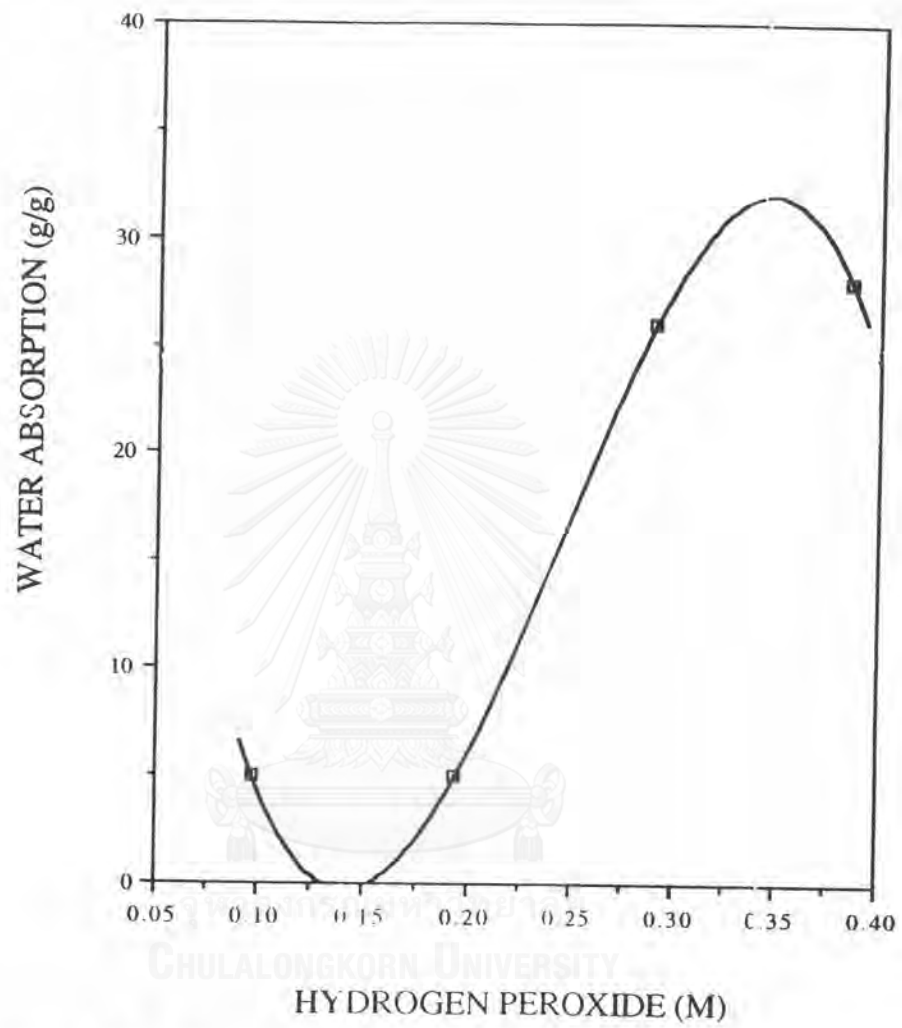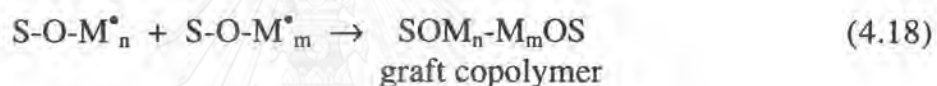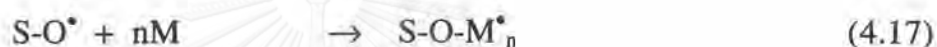percent graft copolymer

Figure 4.9 Effect of hydrogen peroxide concentration on water

absorption of starch-*g*-poly(acrylic acid) copolymer

in deionized distilled water

higher initiator concentration. As a consequence, the number of free radicals on the starch backbone will also increase. It is understandable that these starch macroradicals are formed via a abstraction of the hydrogen atom from starch hydroxyls by the performed free radicals. The probable reactions of H_2O_2 with the monomer and starch are shown in equation 4.15-4.18.

$$H_2O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \tag{4.15}$$

$$S\text{-}OH + {}^{\bullet}OH \rightarrow S\text{-}O^{\bullet} + H_2O \tag{4.16}$$

$$S\text{-}O^{\bullet} + nM \rightarrow S\text{-}O\text{-}M^{\bullet}_n \tag{4.17}$$

$$S\text{-}O\text{-}M^{\bullet}_n + S\text{-}O\text{-}M^{\bullet}_m \rightarrow SOM_n\text{-}M_mOS \tag{4.18}$$
$$\text{graft copolymer}$$
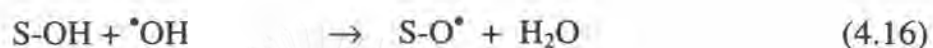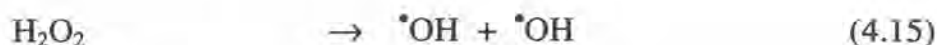
This accounts for the substantial increment in grafting with the hydrogen peroxide concentration up to 1.94×10^{-1}M.

Further increase in H_2O_2 concentration seems to cause a faster decomposition of the H_2O_2, thereby leading to abundance of the free radical species, which in turn, cause a faster rate of termination. Abundance of free radicals may also cease the starch macroradicals as well as growing grafted chain radicals. Stated in other words, the free radical species participate in the initiation as well as the termination of the polymerization reactions, while the free radical species participating in an initiation of grafting reaction gives rise to a higher graft frequency; their participation in a termination reaction decreases which causes graft frequency to decrease accordingly. Current data suggest that the adverse effect of the faster termination using the H_2O_2 concentration higher than 1.94×10^{-1}M is a greater rate of graft initiation.

Beyond this, $^\bullet$OH radicals may largely participate in the termination reaction with the growing polymer chains, thus decreasing the grafting frequency. So water absorption seems to increase gradually when the initiator concentration is higher than 1.94×10^{-1}M. According to the concept of grafting frequency on water absorption capacity, the possible pathways that may occur through the following explanation. As starch is a chunck polymer, it is then regarded as an immobile phase, i.e. acrylic acid is and other small molecules can move or mobile.

The most common case of radical chain polymerization rate to be dependent on the square root of the initiator concentration (13) can be described by eq. 4.19.

$$R_p = k_p\,[M]\left(\frac{fk_d[I]}{k_t}\right)^{1/2} \tag{4.19}$$

Initiator concentration is one of the major attributes to rate of polymerization. At the initiator concentration below 1.94×10^{-1}M, not enough initiator concentration is present for graft copolymerization, resulting in a low grafting frequency in the starch-g-poly(acrylic acid). At the higher concentration of initiator, abundant HO$^\bullet$ radicals are present in the reaction mixture. The radicals can initiate homopolymer of acrylic acid monomer easily than can with the starch chain. This is due to the homopolymer produced is higher than that of graft copolymer as the H_2O_2 concentrations increase (21).

4.3.3 Effect of Amount of Cassava Starch

The effect of amount of starch on percent graft copolymer and the water absorption of the saponified starch-g-poly(acrylic acid)

copolymer in deionized distilled water is tabulated in Table 4.6 and shown in Figures 4.10-4.11, respectively.

TABLE 4.6

Effect of the Amount of Starch on the Saponified

Starch-g-Poly(acrylic acid) Copolymers

Starch (g)[a]	starch:H_2O	%homo- polymer	%graft copolymer	Water absorption in deionized distilled water (g/g)
50	1:12	7.0	91.5	38
60	1:10	4.1	95.9	5
70	1:8.6	4.2	95.8	21
80	1:7.5	4.8	95.2	29

[a]Data were obtained under the following condition: [AA] = 1.70M, [H_2O_2] = 1.94x10^{-1}M, ascorbic acid = 0.33%, reaction time = 3 h, reaction temperature = 35°C

Increasing in the amount of starch charged per batch while keeping the concentrations of H_2O_2 1.94x10^{-1}M, AA 1.70M and water (600 cm^3) constant, is to increase the starch/H_2O_2, starch/AA and starch/water ratios (18). The amount of starch was varied from 50 to 80 g. It is observed in Figure 4.11 that the minimum water absorption is obtained when 60 g of starch was used. Higher or lower than 60 g content brings about the high water absorption. This could be interpreted in terms of: (i) higher concentrations of reactants (starch, acrylic acid and H_2O_2) in the reaction medium at a lower amount of water i.e., a low reaction volume, and (ii) a lower concentration of the reactants in the polymerization medium at a higher amount of water, i.e., a
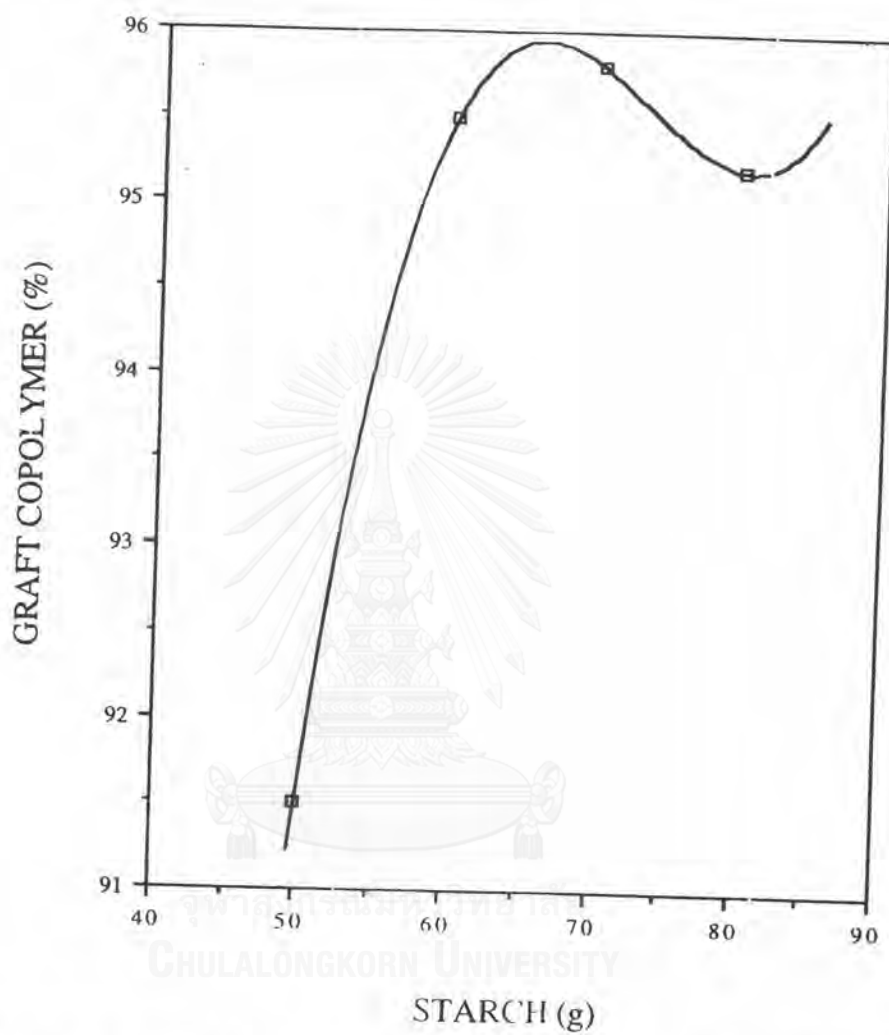
Figure 4.10 Effect of amount of starch on percent graft copolymer
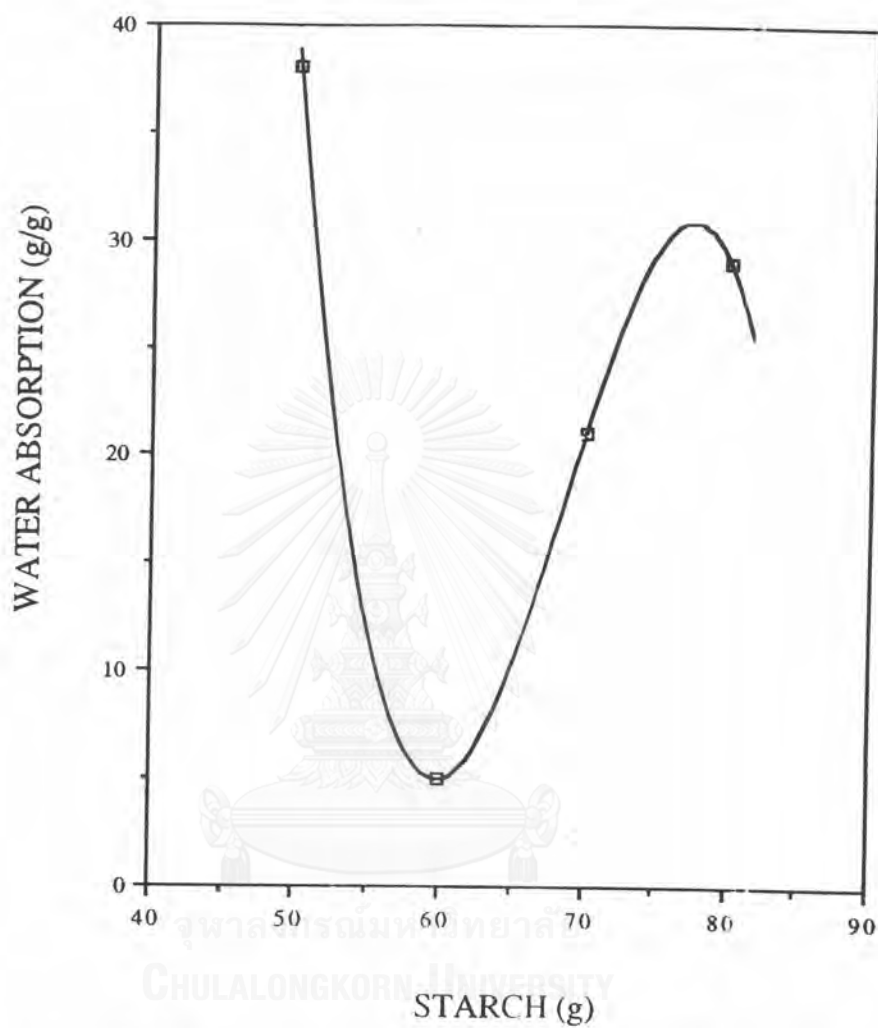
Figure 4.11 Effect of amount of starch on water absorption

of starch-*g*-poly(acrylic acid) copolymer in

deionized distilled water

high reaction volume. The reaction volume affects the freedom degree of movement of reactants, hence the collision probabilities of starch, initiator free radicals and monomer molecules decrease. Also, in the concepts of polymerization, low reaction volume renders an increase amount of starch, that increases the rate of termination and therefore leading to a lower polymerization. The probability of termination reaction of growing polymer chains is increased also by increasing the surface area of the starch molecules. On the other hand, at a high reaction volume i.e., dilution, relativeiy decreases the concentration of starch. The increase in reaction volume seems to enhance the degree of freedom of the reactants and hence increasing the collision probability which gives rise to a higher grafting. Further increase in dilution of the starch decreases the collision probability among reaction ingredients, thereby lowering the grafting.

It is seen that raising the amount of starch from 60 to 80 g brings about a significant decrease in the percent graft copolymer. This might be explanied as: Increasing the amount of starch charged per batch decreased the monomer to starch ratio as that the grafted chains may be decreased.

Current data also suggest that when starch 60 g is used, the reaction molecules have such a degree of freedom of movement, which permits the collision probability among starch, monomer, and initiator molecules. In a high reaction volume, a higher degree of diffusion could be acquired, thereby leading to a maximum grafting. However, at starch/H_2O ratio of 1:10, the minimum water absorption was obtained.

4.3.4 Effect of Ascorbic acid (% weight based on monomer)

The effect of ascorbic acid (percent weight based on the optimum monomer concentration) on percent graft copolymer and the water

absorption of the saponified starch-*g*-poly(acrylic acid) copolymer in deionized distilled water is tabulated in Table 4.7 and shown in Figures 4.12-4.13, respectively.

TABLE 4.7

Effect of the Percentage Ascorbic Acid on the Saponified

Starch-*g*-Poly(acrylic acid) Copolymers

Ascorbic Acid (%)[a]	%homo- polymer	%graft copolymer	Water absorption in deionized distilled water (g/g)
0.16	3.4	96.6	18
0.33	4.1	95.9	5
0.50	6.9	93.1	20
0.67	7.3	92.7	51

[a]Data were obtained under the following condition: [AA] = 1.70M, [H_2O_2] = 1.94×10^{-1}M, starch = 60 g, reaction time = 3 h, reaction temperature = 35°C

The experimental data show that the water absorption decreases until the ascorbic acid concentration increases from 0.16% to 0.33% then it increases when ascorbic acid concentration increases to 0.67%.

The effect of ascorbic acid on the percentage graft copolymer values are best explained in terms of percentage grafting (19). It increases with ascorbic acid concentration within a certain range. In the presence of ascorbic acid, AH$^•$ and $^•$OH radicals generated in the system by the reaction (eqs 4.20-4.24) increase in concentration with increases in percentage of ascorbic acid which may be responsible for the higher rate of grafting.
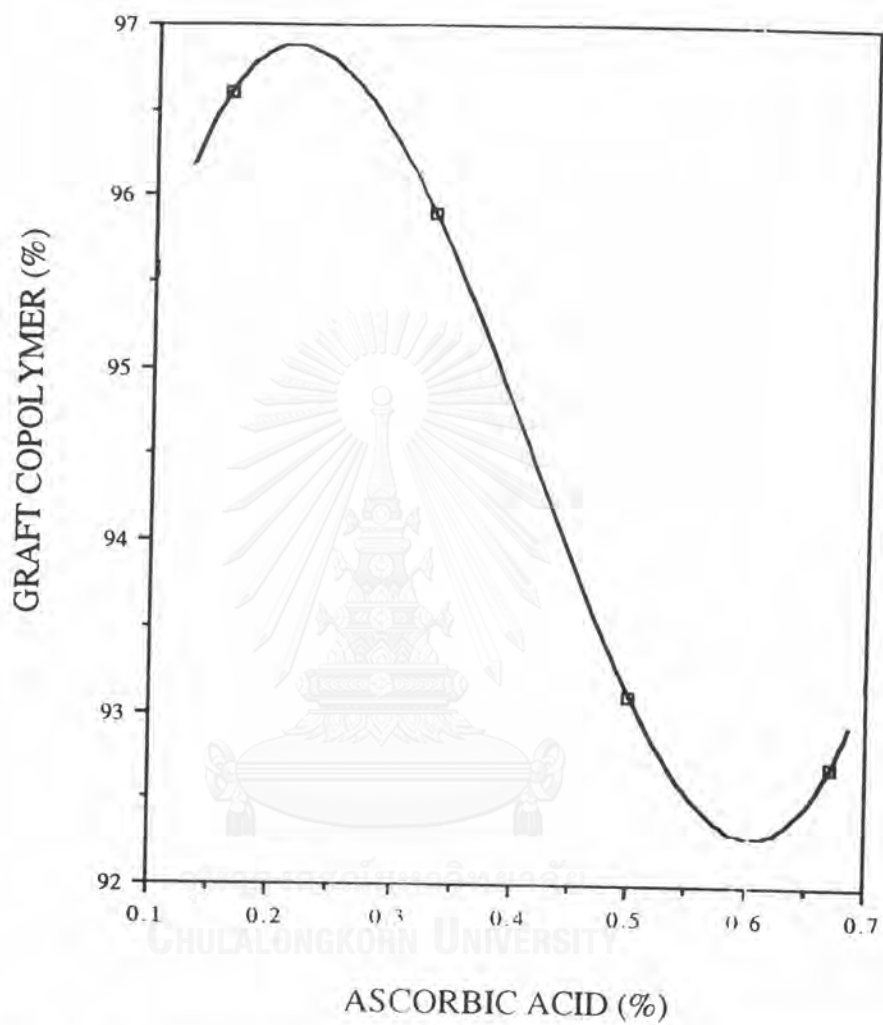
Figure 4.12 Effect of ascorbic acid (%weight based on monomer)
on percent graft copolymer
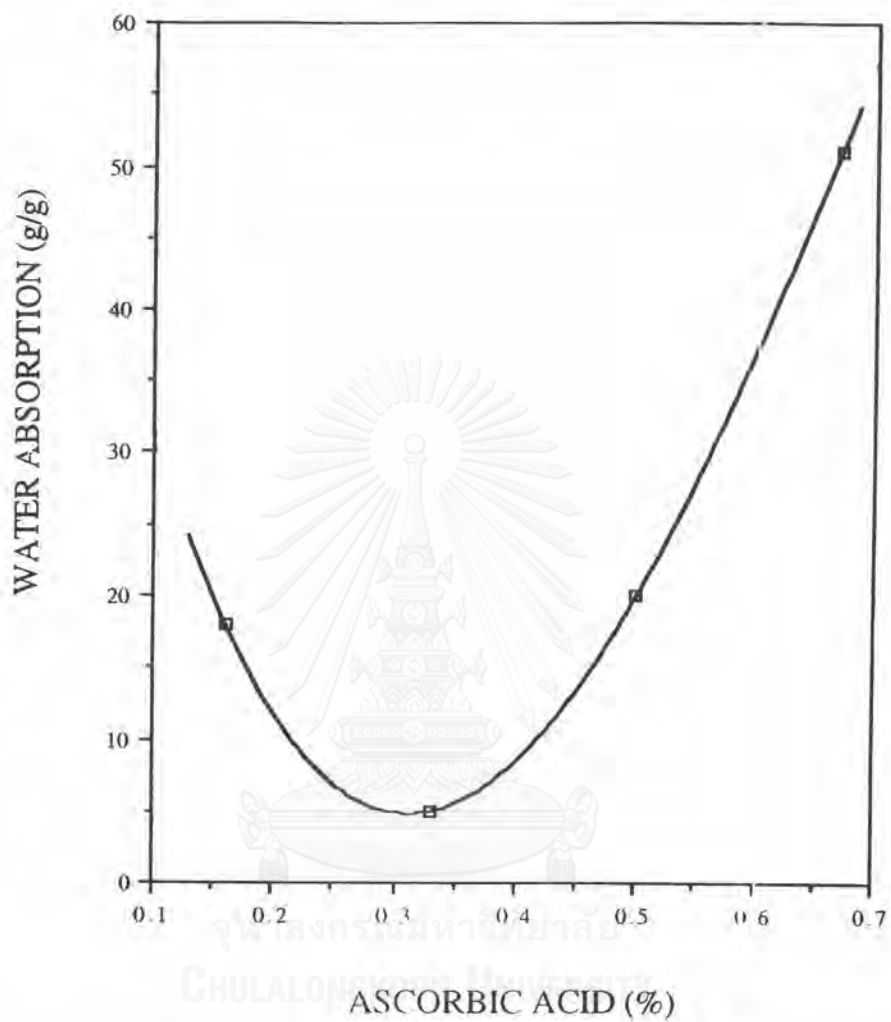
Figure 4.13 Effect of ascorbic acid (% weight based on monomer)
on water absorption of starch-*g*-poly(acrylic acid)
copolymer in deionized distilled water

$$H_2O_2 \quad \rightarrow \quad 2^\bullet OH \qquad (4.20)$$

$$AH_2 \quad \rightarrow \quad AH^- + H^+ \qquad (4.21)$$

$$^\bullet OH + AH^- \quad \rightarrow \quad ^\bullet AH + {}^-OH \qquad (4.22)$$

$$^\bullet AH + H_2O_2 \quad \rightarrow \quad A + {}^-OH + {}^\bullet OH + H^+ \qquad (4.23)$$

$$AH_2 + A \quad \rightarrow \quad 2^\bullet AH \qquad (4.24)$$

$$^\bullet AH + {}^\bullet OH \quad \rightarrow \quad A + {}^-OH + H^+ \qquad (4.25)$$

Initiation

$$M + {}^\bullet OH \text{ or } {}^\bullet AH \quad \rightarrow \quad M^\bullet \qquad (4.26)$$

Propagation

$$M^\bullet + M_{x-1} \quad \rightarrow \quad M_x{}^\bullet \qquad (4.27)$$

$$M^\bullet_{y-1} + M \quad \rightarrow \quad M_y{}^\bullet \qquad (4.28)$$

Termination

$$M^\bullet_x + M_y{}^\bullet \quad \rightarrow \quad M_x\text{-}M_y \qquad (4.29)$$

$$M^\bullet_x + {}^\bullet AH \quad \rightarrow \quad A + M_xH \qquad (4.30)$$
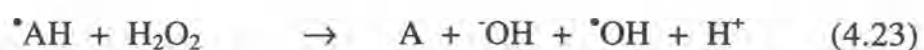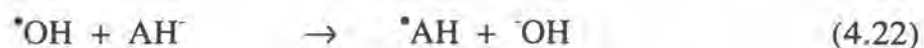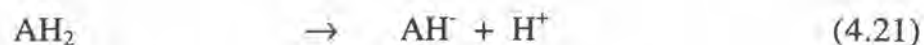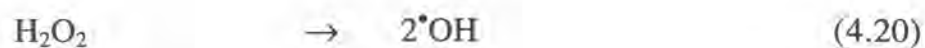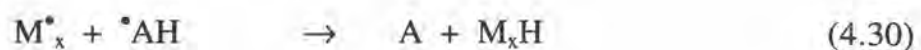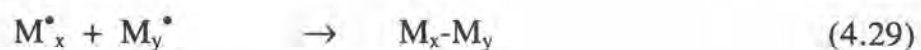
At higher ascorbic acid concentration (0.50-0.67%), a decrease in percent grafting is observed, which may be due to increased formation of hydroxyl ion (eq 4.25).

At low percent ascorbic acid (51), $^{\bullet}$AH radicals formed by eq 4.22 and eq 4.24 concerned mainly by initiation (eq 4.26)and by generating $^{\bullet}$OH radicals (eq 4.23). The $^{\bullet}$OH radicals are an efficient initiator of polymerization; hence the rate of polymerization increases with increasing of ascorbic acid concentration. The pH of the medium makes the rate independence of ascorbic acid by bringing about a sort of reaction balance between the generation and the termination of radical species. The $^{\bullet}$AH radicals are consumed in the termination step (eq 4.25), which assumes to be of greater significance at higher percentage of ascorbic acid. At this stage, degradative termination by eq 4.30 may start competing with eq 4.29. The decrease in the rate at higher percent of ascorbic acid beyond 0.33% is due to excess H^+ ions which induce the catalytic decomposition of H_2O_2 predominantly to give the $^-$OH ion rather than $^{\bullet}$OH radical. This behavior suggests a chain process in the radical generating steps, which involves significant terminations between primary species.

4.3.5 Effect of Reaction Temperature

The effect of reaction temperature on percent graft copolymer and the water absorption of the saponified starch-g-poly(acrylic acid) copolymer in deionized distilled water is tabulated in Table 4.8 and shown in Figures 4.14-4.15, respectively.

The extent of graft copolymerization reaction at 35°C is higher than at 25°C and 30°C that could be associated with increased swell ability of starch and higher mobility of the acrylic acid molecules. Both starch

TABLE 4.8

Effect of the Reaction Temperature on the

Saponified Starch-*g*-Poly(acrylic acid) Copolymers

Temperature (°C)[a]	%homo-polymer	%graft copolymer	Water absorption in deionized distilled water (g/g)
25	6.0	94.0	44
30	4.7	95.3	20
35	4.1	95.9	5
40	6.8	93.3	53

[a]Data were obtained under the following condition: starch = 60 g,

[AA] = 1.70M, [H$_2$O$_2$] = 1.94x10^{-1}M, ascorbic acid = 0.33%,

reaction time = 3 h

swell ability and acrylic acid molecules mobility facilitate absorption of the acrylic acid on the surface of starch, its diffusion inside the swollen starch substrate and its absorption on internal surface, thereby promoting the reaction. It is undoubtedly that starch hydroxyl groups are immobile. The reaction of the hydroxyl groups with acrylic acid would depend on the availability of acrylic acid molecules in their vicinity (23). The lower grafting copolymerization at 40°C than that at 35°C is expected to result from: (i) a faster rate of H$_2$O$_2$ decomposition is significantly high at higher temperatures of the reactor. The decomposition product of H$_2$O$_2$ is the oxygen gas, which is a highly effective radical scavenger due to its inhibition reaction. Besides, the inhibiting effect, the oxygen molecule can additionally oxidized L(+)-ascorbic acid to dehydro-ascorbic acid, a non-reactive species for polymerization (47); (ii) the rate of graft copolymerization decreases due to decreases in monomer and initiator

Figure 4.14 Effect of reaction temperature on percent graft copolymer

Figure 4.15 Effect of reaction temperature on water absorption
of starch-*g*-poly(acrylic acid) copolymer in
deionized distilled water

concentrations in the swollen phase as the rate of consumption of the monomer for the homopolymerization is also higher at higher temperatures in aqueous phase (2).

4.3.6 Effect of Reaction Time

The effect of reaction time on percent graft copolymer and the water absorption of the saponified starch-*g*-poly(acrylic acid) copolymer in deionized distilled water is tabulated in Table 4.9 and shown in Figures 4.16-4.17, respectively.

TABLE 4.9

Effect of the Reaction Time on the Saponified

Starch-*g*-Soly(acrylic acid) Copolymers

Time(h)[a]	%homo-polymer	%graft copolymer	Water absorption in deionized distilled water (g/g)
2	6.5	93.5	41
3	4.1	95.9	5
4	3.7	96.2	28
5	5.5	94.5	37

[a]Data were obtained under the following condition: starch = 60 g, [AA] = 1.70M, [H$_2$O$_2$] = 1.94x10^{-1}M, ascorbic acid = 0.33%, and reaction temperature = 35°C

The experimental data show that the water absorption of starch-*g*-poly(acrylic acid) increases until the reaction time of 3 h, the water absorption then decreased. When the reaction time was longer than 3 h, the
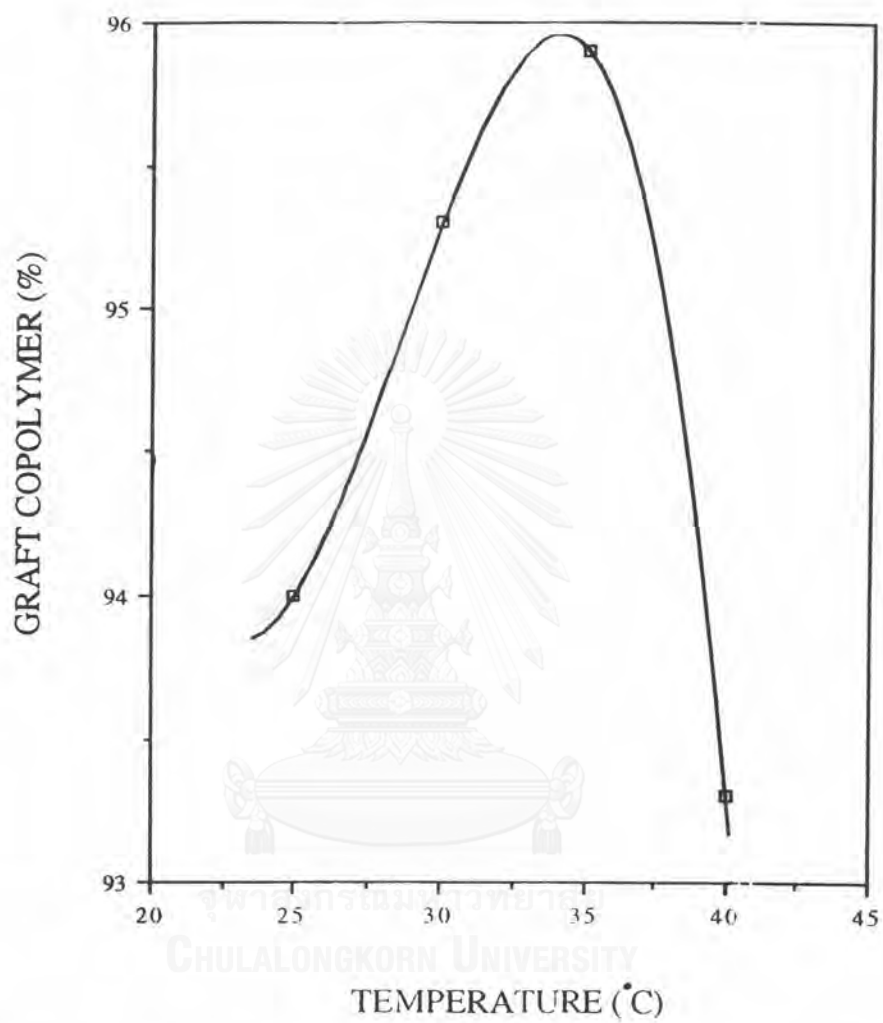
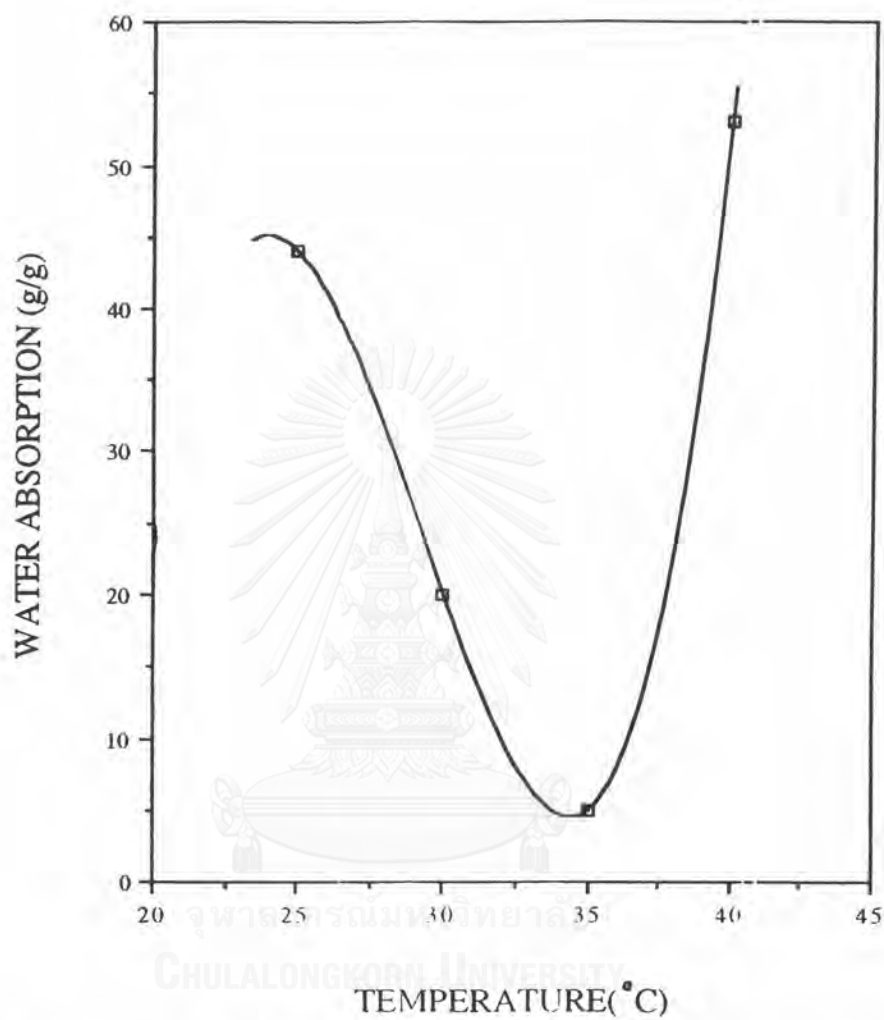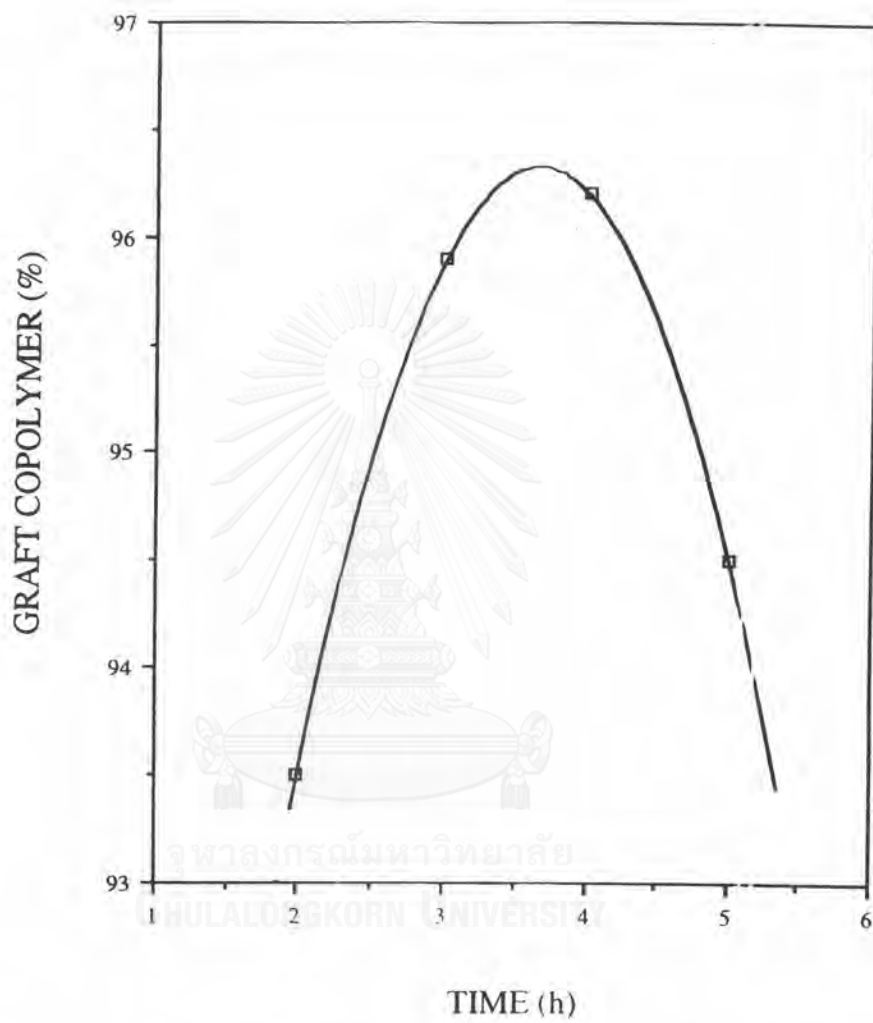Figure 4. 16. Effect of reaction time on percent graft copolymer
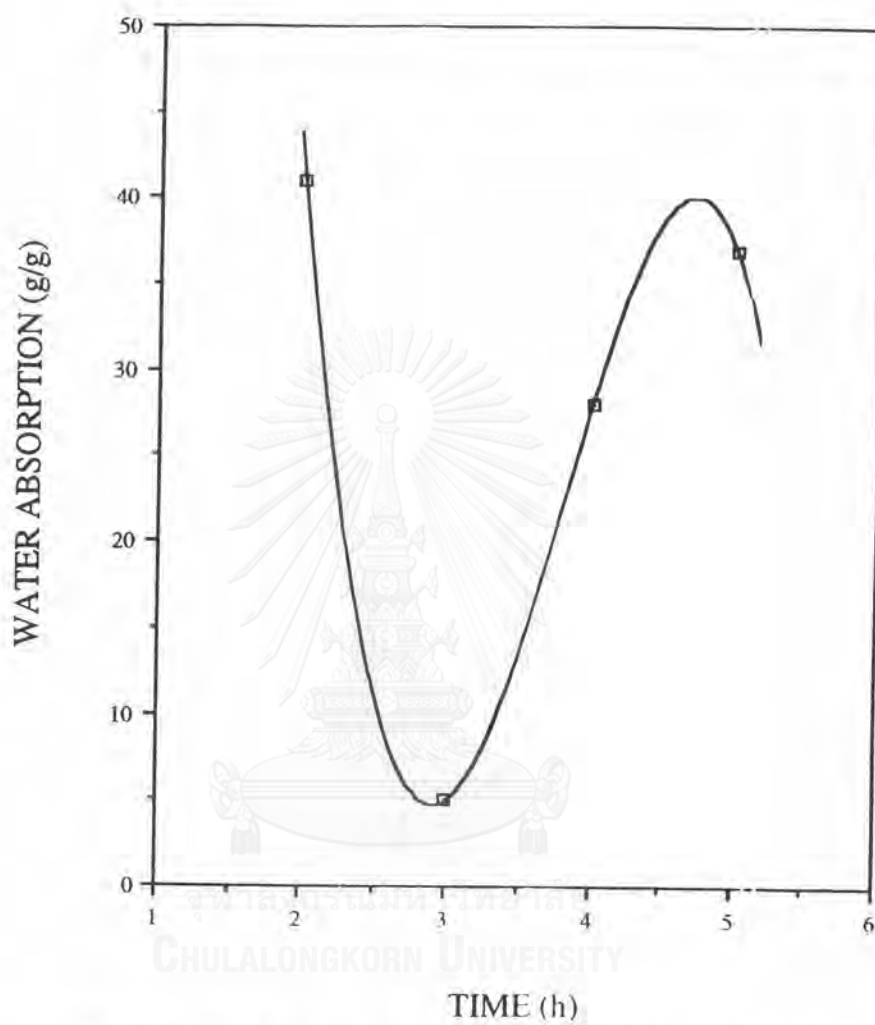
Figure 4.17 Effect of reaction time on water absorption
of starch-g-poly(acrylic acid) copolymer
in deionized distilled water

water absorption increased gradually. The effect of time on water absorption could be explained in terms of grafting frequency of the grafted poly(acrylic acid) on the starch backbone (52).

In the beginning, the rate of grafting increases and reaches a maximum when the reaction time was 3 h. This increase can be explained in two ways: (a) an increase in the length of PAA grafted chains; (b) an increase in the number of grafted chains. These two hypotheses could possibly explained the reasons for the product so obtained for three hours of copolymerization. It is expected that this product with a low water absorption could be used as a thickener of textile printing (29). When the time of reaction proceeds beyond 4 h, the rate then decreases gradually. Slowing down of the rate of grafting as the polymerization proceeds could be attributed to the depletions in monomer and initiation concentrations as well as available active sites on the substrates backbone. However, the reaction time to polymerize takes place during the first 2 h, the rate of grafting increases.

4.3.7 Effect of Addition Rate of Monomer-Initiator Mixture

The effect of addition rate of monomer-initiator mixture on percent graft copolymer and the water absorption of the saponified starch-*g*-poly(acrylic acid) copolymer in deionized distilled water is tabulated in Table 4.10 and shown in Figures 4.18-4.19, respectively.

The experimental data show that the water absorption increases with increasing the addition rate. This result is perhaps explained in terms of increasing the homopolymer content. When the solutions of the monomer and initiator were added in a single portion at the start of polymerization, no new grafting sites were formed in the later stages of the reaction. This suggests that more frequent grafting could be perhaps obtained,

TABLE 4.10

Effect of the Addition Rate of Monomer-Initiator Mixture

on the Saponified Starch-*g*-Poly(acrylic acid) Copolymers

Flow Rate $\times 10^{-2}(cm^3/s)^a$	%homo-polymer	%graft copolymer	Water absorption in deionized distilled water (g/g)
1.67	4.1	95.9	5
2.50	4.4	95.6	10
3.33	5.4	94.6	13
4.17	5.8	94.2	29

[a]Data were obtained under the following condition: starch = 60 g, [AA] = 1.70M, $[H_2O_2]$ = 1.94x10^{-1}M, ascorbic acid = 0.33%, reaction temperature = 35°C, reaction time = 3 h

when both monomer and initiator were added gradually at a controlled rate throughout the course of polymerization. Because of its greater susceptibility to grafting, the gradual addition of monomer and initiator does, indeed, show a slightly higher grafting efficiency than a batch wise addition (53).

Graft copolymerization was carried out by adding a monomer-initiator mixture in a portionwide addition (22, 53), and its average molecular weights were examined. In the reaction, the flow rate of the monomer-initiator mixture is 1.67×10^{-2} cm^3/s was added within a 3 h interval. This portionwide addition gave a higher molecular weight for the grafted poly(acrylic acid) to produce the hydrolyzed starch-*g*-poly(acrylic acid) with a significantly lower water absorbency than the reaction flow rates of 2.50×10^{-2}, 3.33×10^{-2}, and 4.17×10^{-2} cm^3/s. This is due to that homopolymer produced is higher than that of graft copolymer as the reaction flow rate increases.
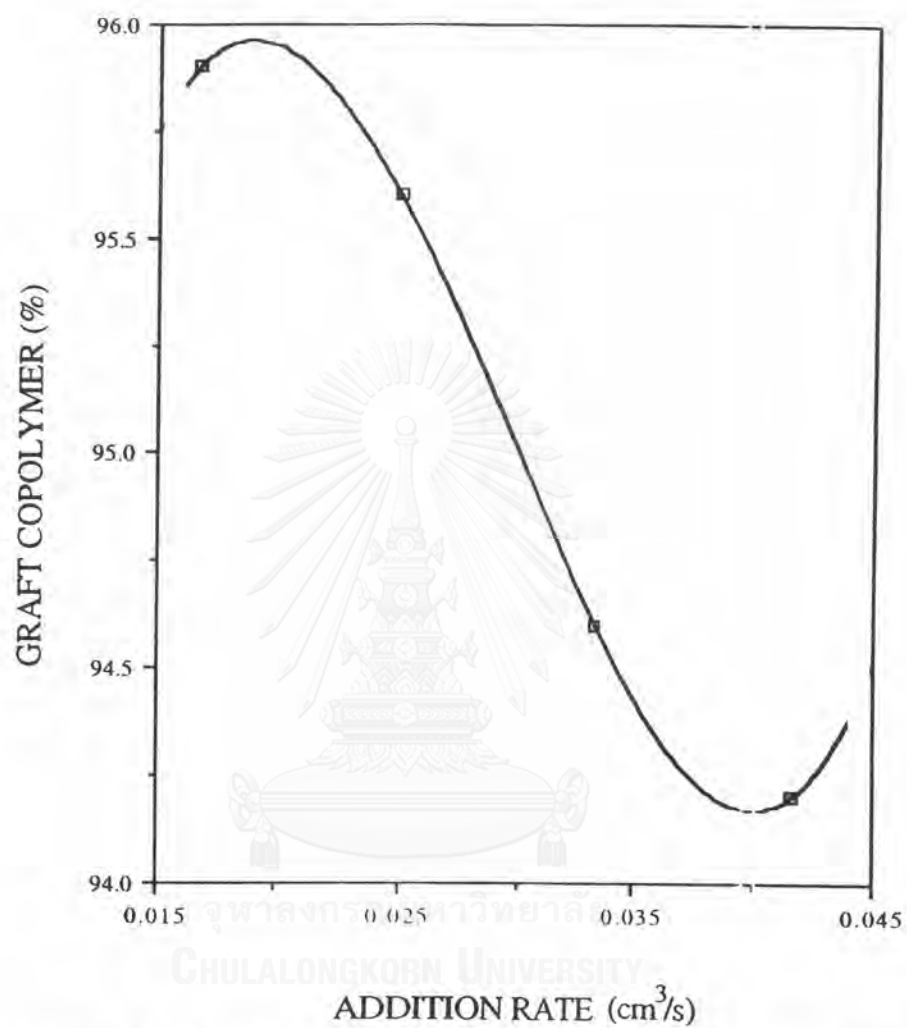
Figure 4.18   Effect of addition rate of monomer-initiator mixture
on percent graft copolymer
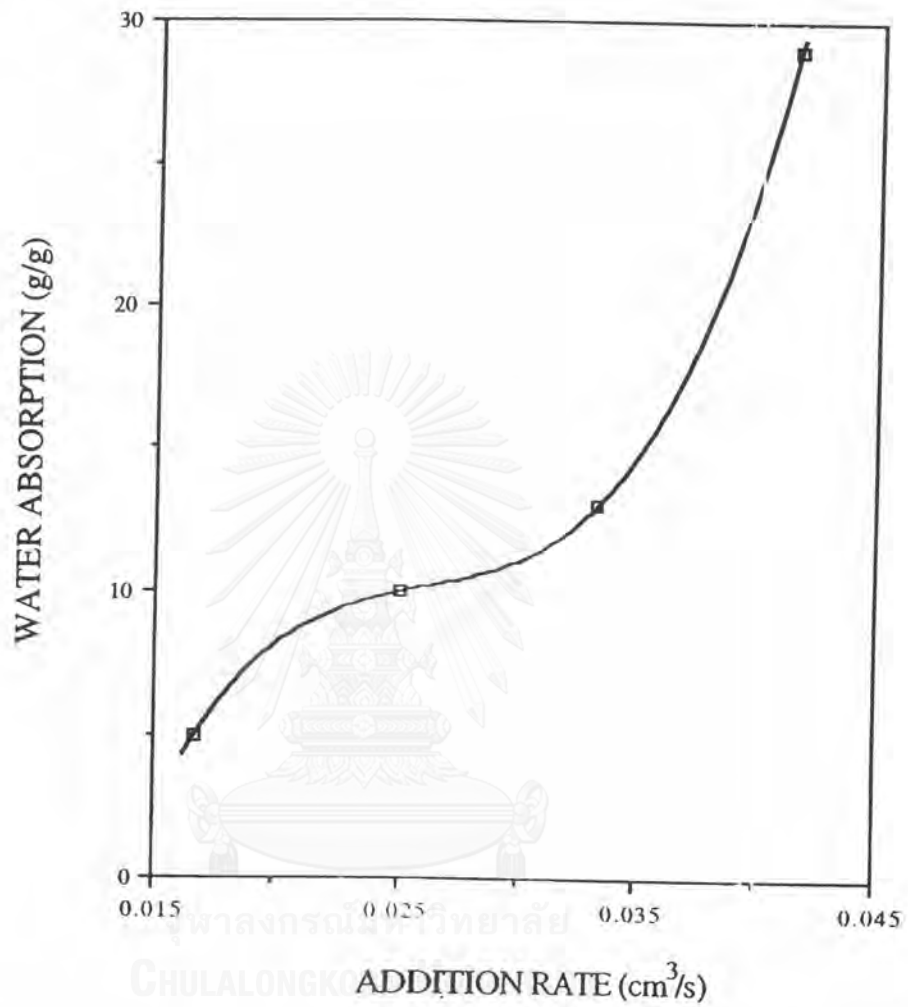
Figure 4.19   Effect of addition rate of monomer-initiator mixture

on water absorption of starch-g-poly(acrylic acid)

copolymer in deionized distilled water

One should not forget that the strong influence of methanol addition rate governs the product sorption ability, i.e. either a high water absorbent or a solution thickener. As mentioned earlier (29), a slow addition and thorough mixing of methanol gave micron-sized gel for a thickener.

4.4   Acid Hydrolysis of Cassava Starch and HSPAA

In this work, there is a difficulty of separating the poly(acrylic acid) grafted chains from the polysaccharide backbone by the enzyme hydrolysis (40) such as α-amylase and acid hydrolysis method, such as sulfuric acid, which is then followed by a precipitation method with a nonsolvent of poly(acrylic acid). By this method, there is no precipitate obtainable from the precipitation method. The acid hydrolysis with glacial acetic acid-perchloric acid, which is a rapid and effective procedure for decomposition, removes the starch moiety with no degradation of grafted polymer. The saponified starch-g-poly(acrylic acid) copolymer and cassava starch have been subjected to an acid hydrolysis procedure in which the hydrolysis of glucosidic linkages take place. Both the linear and branched molecules were possibly hydrolyzed at the α-1-4 and α-1-6 linkages to yield the smaller molecules such as, mono-, di-saccharides. Unfortunately, no recovery of the acrylic polymer chains could possibly be obtained as precipitate. Based on the polarity effect, the poly(sodium acrylate) grafted chains were miscible with water readily (54). Nevertheless, it is essential that the determination of the average molecular weights of the poly(sodium acrylate) grafted chains along with the fragments of starch should be determined by Gel Filtration Chromatography(GFC).

4.5 Techniques for the Determination of the Average Molecular Weights of the Grafted Copolymer

The C-R7A program of GPC file consists of the GPC parameters, which are the setting of basic calculation parameters. The GPC basic parameters consist of channels (RID, UV), average molecular weights($\overline{M}_W$, $\overline{M}_N$, $\overline{M}_V$, $\overline{M}_Z$), and intrinsic viscosity, stop time, initial time, Q-Factor, alpha, and kappa values. In this case, the values of Q-Factor (QF = 1), alpha ($\alpha = 0.64$), and kappa ($\kappa = 0.64$) are essential for the calculation of average molecular weights. They must be selected properly for each system depending on the system and structure of the polymer studied (Appendix A).

4.5.1 Effect of Fow Rate of the Mobile Phase

In this research, a flow rate of mobile phase was also variable. Two levels of the flow rate under investigation are 8.33×10^{-3} and 1.67×10^{-2} cm^3/s. The retention times of Shodex standard P-82 (Pullulan) as P-1600, P-400, P-200, P-100, P-50, and P-5, with the average molecular weights of 1,660,000, 380,000, 186,000, 100,000, 48,000, and 5,800 for the corresponding flow rate of the mobile phase of 8.33×10^{-3} cm^3/s are 32.62, 33.49, 36.45, 38.37, 44.87 and 59.68 minutes, respectively. In contrast, when the flow rate of the same mobile phase for the Shodex standard is 1.67×10^{-2} cm^3/s, the retention times are 15.65, 16.75, 17.68, 19.82, 21.98, and 30.63 minutes, respectively. Since the flow rate at 8.33×10^{-3} cm^3/s is, of course, slower than that at 1.67×10^{-2} cm^3/s as a factor of a half, it provides approximately twice the long retention times, which is clearly shown in Figures 4.20-4.21.

The hydrolyzed cassava starch and the hydrolyzed HSPAA, which are also run with both flow rates of mobile phase at both 8.33×10^{-3} and
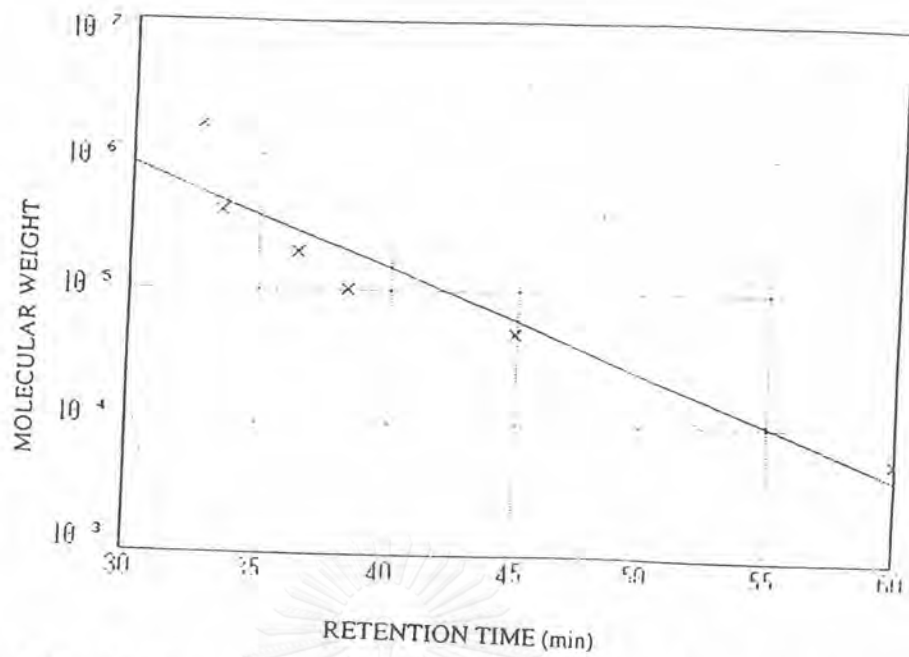
Figure 4.20 The molecular weight calibration curve of P-82 Pullulan standard with the flow rate of the mobile phase of 8.33×10^{-3} cm^3/s
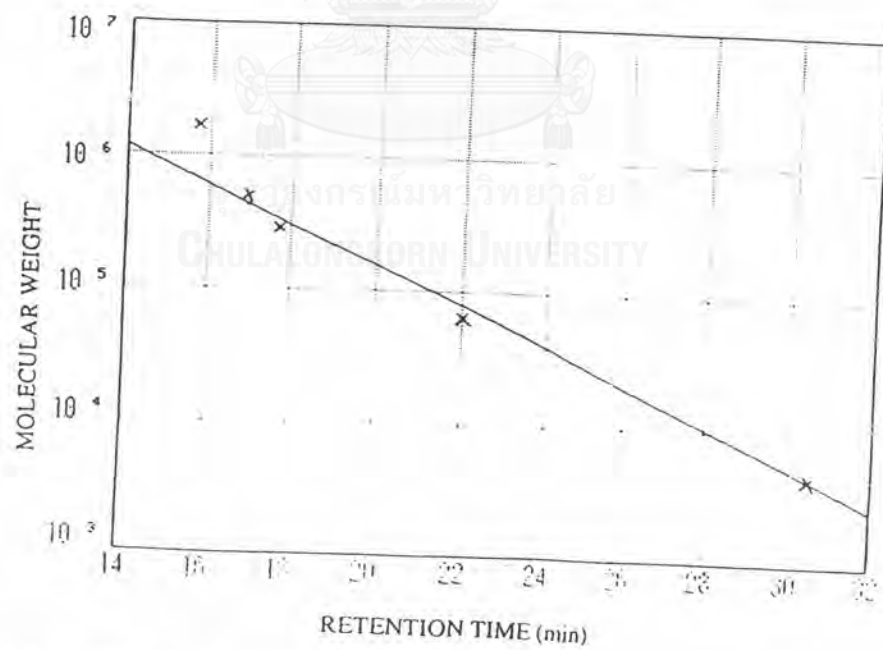
Figure 4.21 The molecular weight calibration curve of P-82 Pullulan standard with the flow rate of the mobile phase of 1.67×10^{-2} cm^3/s

$1.67\text{x}10^{-2}$ cm^3/s. The GFC chromatographs obtained from the Baseline C-R7A software are shown in Figures 4.22-4.25. It can be seen that Figures 4.22, and 4.24 represent the GFC chromatographs of the hydrolyzed cassava starch and the hydrolyzed HSPAA with the flow rate of the mobile phase of $8.33\text{x}10^{-3}$ cm^3/s. Figures 4.23, and 4.25 show the GFC chromatographs of the hydrolyzed cassava starch and the hydrolyzed HSPAA with $1.67\text{x}10^{-2}$ cm^3/s of the flow rate of the mobile phase. Considerable separation of the peaks could be observed with the flow rate of $8.33\text{x}10^{-3}$ cm^3/s, the peaks in Figures 4.22 and 4.24 can be separated somewhat better than those in Figures 4.23 and 4.25 in terms of the peak bandwidth. Thus the flow rate of the mobile phase at $8.33\text{x}10^{-3}$ cm^3/s is then used.

The peak data of the hydrolyzed cassava starch and the hydrolyzed saponified starch-g-poly(acrylic acid) copolymers were shown in Tables 4.11-4.18, and Appendix B.

One can see clearly that the starch was acid hydrolyzed into oligosaccharides with $\overline{M}_w$, $\overline{M}_n$, $\overline{M}_v$ and $\overline{M}_z$ of 1,005, 1,002, 1,005, 1,008, respectively. One interesting feature found is the monodispersity of the average-molecular weights of each fraction of the starch by the acid hydrolysis. This result implies that the mixture of glacial acetic acid (100 cm^3) and 60% perchloric acid (2 cm^3) cleaves certain reactive sites of the polysaccharide into many different products. All are of small molecules. Based on the molecular weight of a glucose unit of 162, the number of the cleaved products contains 6.2, 1.9, and 1.2 glucose units. As mentioned above, the monodispersity ($\overline{M}_w/\overline{M}_n$) of the products suggests a somewhat equal distribution of weight and number-average molecular weights of each fraction. For the molecular weight average of the starch as a whole is 235 with a polydisperse index of 1.22.
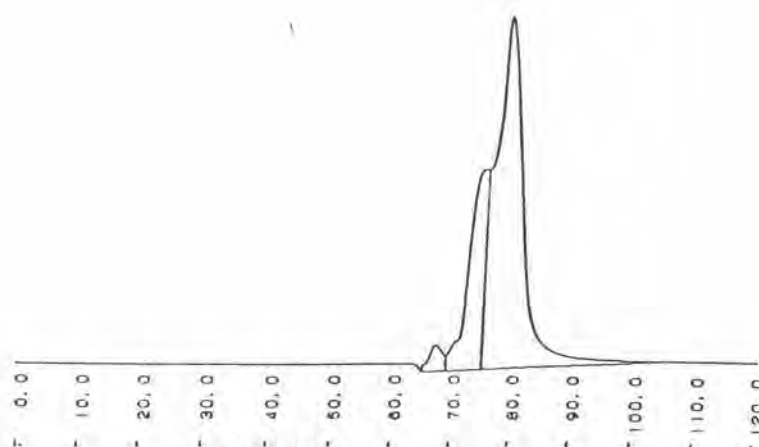
Figure 4.22   The GFC chromatograph of the acid hydrolyzed cassava starch with the flow rate of the mobile phase of 8.33×10^{-3} cm^3/s

RETENTION TIME (min)
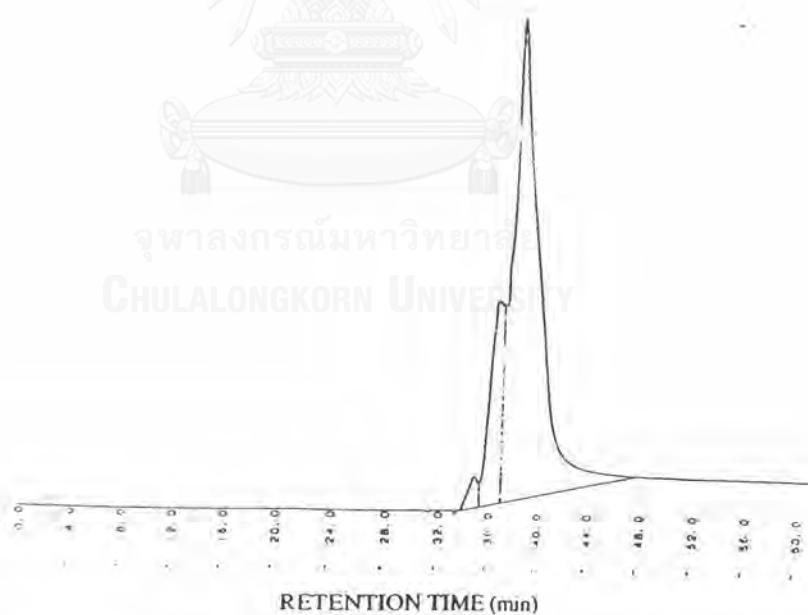
Figure 4.23   The GFC chromatograph of the acid hydrolyzed cassava starch with the flow rate of the mobile phase of 1.67×10^{-2} cm^3/s

RETENTION TIME (min)
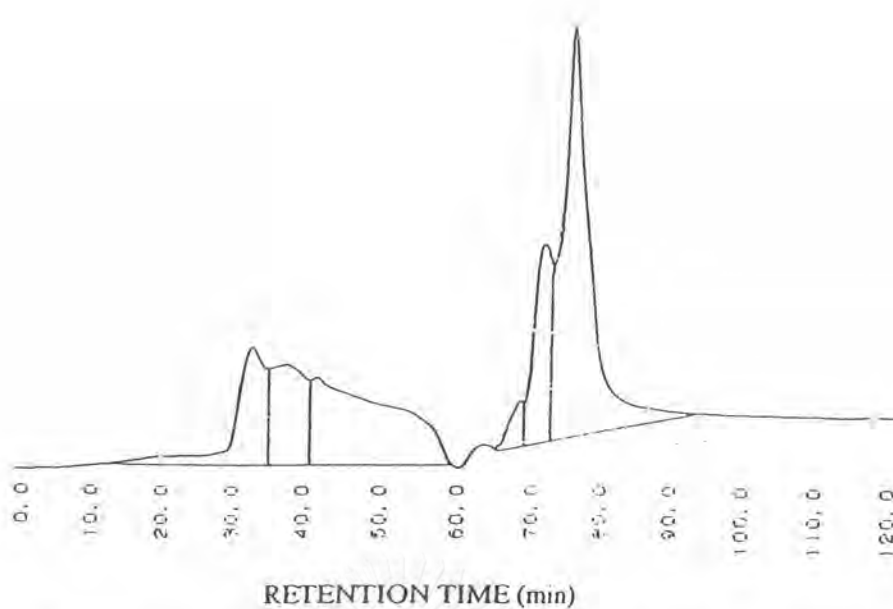
Figure 4.24   The GFC chromatograph of the acid hydrolyzed
starch-g-poly(acrylic acid) with the flow rate of
the mobile phase of 8.33×10^{-3} cm^3/s

RETENTION TIME (min)
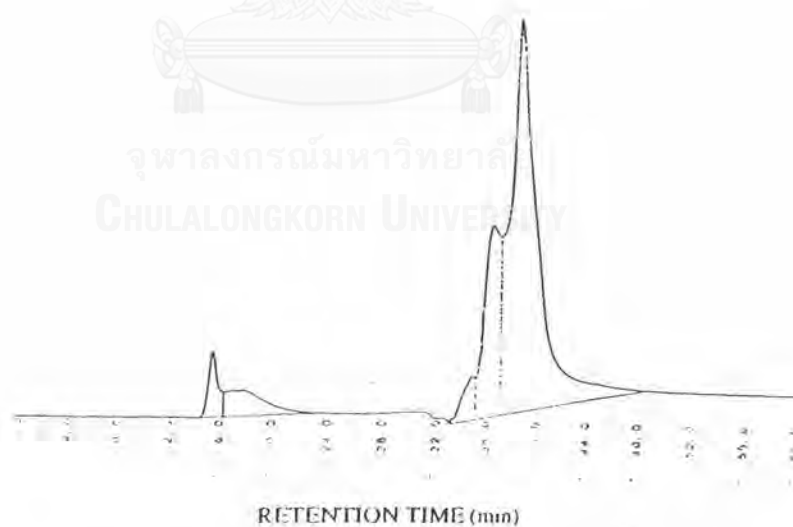
Figure 4.25   The GFC chromatograph of the acid hydrolyzed
starch-g-poly(acrylic acid) with the flow rate of
the mobile phase of 1.67×10^{-2} cm^3/s

Table4.11

Effect of Acid Hydrolysis of Starch on Average Molecular Weights in
The Gel Filtration Chromatographic Peaks

Property	Starch			
	peak 1	peak 2	peak 3	Total peak
peak start (min)	66.94	73.99	75.69	66.94
peak top (min)	68.38	75.49	78.44	78.44
peak end (min)	68.70	75.69	79.94	79.94
$\overline{M}_w$	1,005	302	190	253
$\overline{M}_n$	1,002	300	184	207
$\overline{M}_v$	1,005	301	189	240
$\overline{M}_z$	1,008	303	197	388
$(\overline{M}_w/\overline{M}_n)$	1.00	1.01	1.04	1.22
$(\overline{M}_v/\overline{M}_n)$	1.00	1.00	1.03	1.16
$(\overline{M}_z/\overline{M}_w)$	1.00	1.01	1.04	1.53
I.VISC	53.39	24.71	18.34	21.33

For the saponified starch graft copolymers, the GFC peaks and data of these graft copolymers had a variety of retention times. The molecular weight averages and their distributions of the polyacrylate itself are interesting. Because the polydispersity is rather monodisperse ($\overline{M}_w/\overline{M}_n$=1) for each fraction separated. As for the total value of poly-dispersity, the index varies from 1.11 to 8.99, which indicates that the average molecular weight distribution is polydispersed. Such a property of molecular weight average implies that the material possesses a board range of thermal transitions (see Appendix C). Unfortunately, the confirmation of the chemical reactions occurred during the acid hydrolysis could not be carried out at this moment. In the view of the work of Gurruchaga et.al (39), changes in the weight of the recovered chains were obtained so as to make hypothesis that a new ester could be produced by transesterification in either routes of intramolecular, intermolecular with another polymer chain, or intermolecular with acetic acid solvent. For the present case, the recovery of the acrylic polymer side chain (polyacrylate) is relatively difficult because its sodium salt is readily soluble in water. Evaporation of the aqueous phase or freeze drying of the product may be possible for a recovery of the grafted salt of poly(acrylic acid), which can be carried out as the future trial and error experiments.

The average molecular weights (3,887-89,022, and 101,246-651,967) obtained from the GFC experiments suggest that the fragments should contain the grafted polyacrylate. As the molecular weight of the($-CH_2-CH-COONa-$) is 98, and if the molecular weight obtained (651,967) were for the grafted polyacrylate, then it would have contained at least 6,653 units of sodium acrylate monomer that it should have been strongly soluble in water because it is a gaint ionic salt.

Table 4.12

Effect of Concentration of Acrylic Acid on Average Molecular Weights of the Graft PAA in The Gel Filtration Chromatographic Peaks

Property	Acrylic Acid [M]											
	1.70*			2.06**			2.40***			2.73****		
	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak
peak start (min)	30.50	NA	30.50	30.25	33.30	30.25	31.30	33.60	31.20	21.30	36.20	21.30
peak top (min)	32.18	NA	32.18	32.79	35.32	35.32	32.40	36.11	36.11	33.73	38.58	33.73
peak end (min)	33.50	NA	33.50	33.30	42.00	56.80	33.00	52.65	52.65	36.20	42.00	42.00
$\overline{M}_w$	583,262	NA	583,262	543,338	251,550	209,951	525,767	197,292	220,143	651,967	176,114	357,495
$\overline{M}_n$	578,412	NA	578,412	538,114	213,967	84,621	520,927	119,474	126,242	464,607	161,988	297,961
$\overline{M}_v$	582,383	NA	582,383	542,358	244,840	188,767	524,884	185,197	204,629	594,068	173,526	346,735
$\overline{M}_z$	588,174	NA	588,174	548,968	287,986	318,770	530,709	256,853	302,354	1,222,646	190,588	414,416
$(\overline{M}_w/\overline{M}_n)$	1.01	NA	1.01	1.01	1.18	2.48	1.01	1.65	1.74	1.40	1.09	1.21
$(\overline{M}_v/\overline{M}_n)$	1.01	NA	1.01	1.01	1.14	2.23	1.01	1.55	1.62	1.28	1.07	1.18
$(\overline{M}_z/\overline{M}_w)$	1.01	NA	1.01	1.01	1.14	1.52	1.01	1.30	1.37	1.88	1.08	1.16
I.VISC	3,132.66	NA	3,132.66	2,933.11	1,799.13	1,523.26	2,931.03	1,504.75	1,603.98	3,172.74	1,443.35	2,247.89

*graft copolymer 95.9%, **graft copolymer 93.3%, ***graft copolymer 90.3%, ****graft copolymer 87.7%, NA = not available.

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Table 4.13

Effect of Concentration of Hydrogen Peroxide on Average Molecular Weights of the Graft PAA in The Gel Filtration ChromatographicPeaks

Property	Hydrogen Peroxide [M]											
	9.70x10^-2*			1.94x10^-1**			2.90x10^-1***			3.86x10^-1****		
	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak
peak start (min)	29.90	42.30	29.00	30.50	NA	30.50	33.40	35.35	33.40	34.30	40.45	34.30
peak top (min)	32.54	42.97	32.54	32.18	NA	32.18	35.00	36.59	36.59	36.08	55.46	55.46
peak end (min)	42.30	53.10	53.10	33.50	NA	33.50	35.35	42.55	42.25	40.05	61.85	61.85
$\bar{M}_w$	372,641	59,710	60,949	583,262	NA	583,262	369,813	232,524	263,505	269,099	18,700	53,958
$\bar{M}_n$	288,330	50,772	52,464	578,412	NA	578,412	367,580	219,267	241,231	259,044	11,372	13,141
$\bar{M}_v$	357,720	58,279	59,579	582,383	NA	582,383	369,403	230,281	259,593	267,333	16,906	38,144
$\bar{M}_z$	448,297	66,946	67,912	588,174	NA	588,174	372,121	244,376	284,833	278,723	32,623	205,443
$(\bar{M}_w/\bar{M}_n)$	1.32	1.18	1.16	1.01	NA	1.01	1.01	1.06	1.09	1.04	1.64	4.11
$(\bar{M}_v/\bar{M}_n)$	1.26	1.15	1.14	1.01	NA	1.01	1.00	1.05	1.08	1.03	1.49	2.91
$(\bar{M}_z/\bar{M}_w)$	1.20	1.12	1.11	1.01	NA	1.01	1.01	1.05	1.08	1.04	1.74	3.81
I.VISC	2,293.23	717.97	728.18	3,132.66	NA	3,132.66	2,340.88	1,729.92	1,867.79	1,903.24	352.18	547.39

*graft copolymer 92.9%, **graft copolymer 95.9%, ***graft copolymer 93.5%, ****graft copolymer 93.2%, NA = not available.

Table 4.14

Effect of Amount of Starch on Average Molecular Weights of the Graft PAA in The Gel Filtration Chromatographic Peaks

Property	Starch (g)											
	50*			60**			70***			80****		
	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	pcak 2	total peak	peak 1	peak 2	total peak
peak start (min)	30.65	33.85	30.65	30.50	NA	30.50	31.70	33.50	31.70	31.15	34.05	31.15
peak top (min)	32.94	37.06	47.04	32.18	NA	32.18	32.40	36.11	36.11	32.63	36.51	56.98
peak end (min)	33.85	39.35	61.88	33.50	NA	33.50	33.50	42.95	42.95	34.05	42.35	61.05
$\bar{M}_w$	509,498	263,328	108,541	583,262	NA	583,262	523,306	263,934	243,365	517,270	249,907	164,878
$\bar{M}_n$	503,589	245,096	25,144	578,412	NA	578,412	520,103	238,153	138,424	511,978	229,473	18,339
$\bar{M}_v$	508,401	259,944	85,709	582,383	NA	582,383	522,727	259,661	226,851	516,320	246,423	126,833
$\bar{M}_z$	515,741	282,440	268,159	588,174	NA	588,174	526,516	286,374	324,576	522,532	268,540	348,394
$(\bar{M}_w/\bar{M}_n)$	1.01	1.07	4.13	1.01	NA	1.01	1.01	1.11	1.88	1.01	1.09	8.99
$(\bar{M}_v/\bar{M}_n)$	1.01	1.06	3.41	1.01	NA	1.01	1.01	1.09	1.64	1.01	1.07	6.92
$(\bar{M}_z/\bar{M}_w)$	1.01	1.07	2.47	1.01	NA	1.01	1.01	1.09	1.34	1.01	1.07	2.11
I.VISC	2,871.78	1,869.40	918.99	3,132.66	NA	3,132.66	2,923.31	1,868.09	1,713.38	2,900.33	1,806.57	1,180.99

*graft copolymer 91.5%, **graft copolymer 95.9%, ***graft copolymer 95.8%, ****graft copolymer 95.2%, NA = not available.

Table 4.15

Effect of Concentration of Ascorbic Acid on Average Molecular Weights of the Graft PAA in The Gel Filtration Chromatographic Peaks

Property	Ascorbic Acid (%)											
	0.16*			0.33**			0.50***			0.67****		
	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak
peak start (min)	30.60	30.05	30.60	30.50	NA	30.50	27.15	36.15	27.15	33.70	43.00	33.70
peak top (min)	32.69	40.83	52.39	32.18	NA	32.18	32.80	38.01	32.80	34.45	43.30	34.45
peak end (min)	30.05	44.95	61.55	33.50	NA	33.50	36.15	52.55	58.55	43.00	45.30	60.00
$\bar{M}_w$	495,714	173,286	142,135	583,262	NA	583,262	516,135	107,009	338,433	231,539	70,116	214,332
$\bar{M}_n$	481,221	147,322	30,057	578,412	NA	578,412	471,584	56,903	174,537	187,715	69,174	852,274
$\bar{M}_v$	493,105	168,370	113,911	582,383	NA	582,383	507,186	97,403	312,356	233,566	69,946	188,427
$\bar{M}_z$	510,201	201,488	323,398	588,174	NA	588,174	572,586	158,623	464,146	274,914	71,053	359,734
$(\bar{M}_w/\bar{M}_n)$	1.03	1.18	4.73	1.01	NA	1.01	1.09	1.88	1.94	1.23	1.01	2.51
$(\bar{M}_v/\bar{M}_n)$	1.02	1.14	3.79	1.01	NA	1.01	1.08	1.71	1.79	1.19	1.01	2.34
$(\bar{M}_z/\bar{M}_w)$	1.03	1.16	2.28	1.01	NA	1.01	1.11	1.48	1.37	1.19	1.01	1.68
I.VISC	2,816.18	1,415.76	1,102.51	3,132.66	NA	3,132.66	2,867.39	997.39	2,102.59	1,697.46	806.92	1,521.49

*graft copolymer 96.6%, **graft copolymer 95.9%, ***graft copolymer 93.1%, ****graft copolymer 92.7%, NA = not available.

Table 4.16

Effect of Reaction Temperature on Average Molecular Weights of the Graft PAA in The Gel Filtration Chromatographic Peaks

Property	Temperature (°C)											
	25*			30**			35***			40****		
	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak
peak start (min)	25.90	41.75	25.90	31.90	41.95	31.90	30.50	NA	30.50	32.65	34.05	32.65
peak top (min)	39.01	42.77	39.01	36.71	42.88	36.71	32.18	NA	32.18	33.07	37.25	55.52
peak end (min)	41.75	60.45	60.45	41.95	60.35	60.35	33.50	NA	33.50	34.00	29.50	61.60
$\bar{M}_w$	239,731	42,338	123,212	238,838	40,667	133,972	583,262	NA	583,262	480,377	253,461	39,371
$\bar{M}_n$	194,695	23,454	36,667	200,405	22,785	39,103	578,412	NA	578,412	479,342	241,038	13,032
$\bar{M}_v$	229,283	38,861	103,013	231,390	37,320	113,932	582,383	NA	582,383	480,190	251,220	29,692
$\bar{M}_z$	322,104	60,869	269,116	282,590	58,685	246,624	588,174	NA	588,174	481,401	265,882	150,575
$(\bar{M}_w/\bar{M}_n)$	1.23	1.81	3.36	1.19	1.78	3.43	1.01	NA	1.01	1.00	1.05	3.02
$(\bar{M}_v/\bar{M}_n)$	1.18	1.66	2.89	1.15	1.64	2.91	1.01	NA	1.01	1.00	1.04	2.28
$(\bar{M}_z/\bar{M}_w)$	1.34	1.44	2.18	1.18	1.44	1.84	1.01	NA	1.01	1.00	1.05	3.82
I.VISC	1,725.11	553.94	1,033.78	1,735.24	539.78	1,102.64	3,132.66	NA	3,132.66	2,768.75	1,829.00	466.30

*graft copolymer 94.0%, **graft copolymer 95.9%, ***graft copolymer 93.3%, ****graft copolymer 95.3%, NA = not available.

Table 4.17

Effect of Reaction Time on Average Molecular Weights of the Graft PAA in The Gel Filtration Chromatographic Peaks

Property	Reaction Time (h)											
	2*			3**			4***			5****		
	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak
peak start (min)	31.20	33.90	31.20	30.50	NA	30.50	30.45	39.65	30.45	31.15	33.90	31.15
peak top (min)	33.05	47.46	47.46	32.18	NA	32.18	32.74	43.62	32.73	33.20	36.28	36.28
peak end (min)	33.90	61.60	61.60	33.50	NA	33.50	39.65	44.65	59.85	33.90	42.2	61.70
$\bar{M}_w$	497,003	77,459	87,653	583,262	NA	583,262	376,937	79,352	221,611	508,912	234,051	141,783
$\bar{M}_n$	492,353	23,644	24,197	578,412	NA	578,412	325,698	78,061	41,090	502,224	200,500	25,649
$\bar{M}_v$	496,147	63,557	70,248	582,383	NA	582,383	368,090	79,117	184,917	507,674	228,020	112,054
$\bar{M}_z$	501,843	174,188	219,507	588,174	NA	588,174	423,797	80,657	393,237	515,925	266,943	313,307
$(\bar{M}_w/\bar{M}_n)$	1.01	3.28	3.62	1.01	NA	1.01	1.16	1.02	5.39	1.01	1.17	5.53
$(\bar{M}_v/\bar{M}_n)$	1.01	2.69	2.90	1.01	NA	1.01	1.13	1.01	4.50	1.01	1.14	4.37
$(\bar{M}_z/\bar{M}_w)$	1.01	2.25	2.50	1.01	NA	1.01	112	1.02	1.77	1.01	1.14	2.22
I.VISC	2,827.29	758.93	809.14	3,132.66	NA	3,132.66	2,335.55	873.12	1,503.29	2,869.16	1,719.03	1,090.97

*graft copolymer 93.5%, **graft copolymer 95.9%, ***graft copolymer 96.3%, ****graft copolymer 94.5%, NA = not available.

Table 4.18

Effect of Addition Rate of Monomer-Initiator Mixture on Average Molecular Weights of the Graft PAA inThe Gel Filtration Chromatographic Peaks

Property	Addition Rate (cm³/s)											
	0.0167*			0.0250**			0.0333***			0.0417****		
	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak	peak 1	peak 2	total peak
peak start (min)	30.50	NA	30.50	30.90	41.85	30.90	22.65	NA	22.65	27.35	42.10	27.35
peak top (min)	32.18	NA	32.18	34.87	42.63	34.87	37.10	NA	37.10	35.67	42.43	35.67
peak end (min)	33.50	NA	33.50	41.85	58.95	58.95	59.80	NA	59.80	42.10	56.00	56.00
$\overline{M}_w$	583,262	NA	583,262	311,536	46,954	255,769	255,895	NA	255,895	282,938	55,230	224,018
$\overline{M}_n$	578,412	NA	578,412	249,337	28,041	70,141	73,755	NA	73,755	225,957	41,063	104,540
$\overline{M}_v$	582,383	NA	582,383	300,146	43,336	199,551	211,102	NA	211,102	271,539	52,965	204,347
$\overline{M}_z$	588,174	NA	588,174	374,766	63,415	353,965	668,798	NA	668,798	354,688	66,508	330,297
$(\overline{M}_w/\overline{M}_n)$	1.01	NA	1.01	1.25	1.66	3.22	3.47	NA	3.47	1.25	135	2.14
$(\overline{M}_v/\overline{M}_n)$	1.01	NA	1.01	1.20	1.55	1.57	2.86	NA	2.86	1.20	1.29	1.95
$(\overline{M}_z/\overline{M}_w)$	1.01	NA	1.01	1.20	1.36	2.85	2.61	NA	2.61	1.25	1.20	1.47
I.VISC	3,132.66	NA	3,132.66	2,049.61	593.97	1,578.39	1,636.27	NA	1,636.27	1,922.35	675.35	1,602.56

*graft copolymer 95.9%, **graft copolymer 95.6%, ***graft copolymer 94.6%, ****graft copolymer 94.2%, NA = not available.

However, it is of great interest to observe the relationship between the molecular weight average of the graft copolymer and the quality of printed cotton fabrics. This should be recommended for future work.

The intrinsic viscosity $[\eta]$ is confined to different molecular weights of a given polymer. The relationship between the intrinsic viscosity/viscosity-average molecular weight is governed by the Mark-Houwink equation. The data of GFC in Tables 4.12-4.18, which show that the intrinsic viscosity usually increases with an increase of molecular weight of the product. Thus the intrinsic viscosity of the polymer increases as the reaction mixture contains longer chains of the polymer in solution and resulting in the larger molecular weight polymer. The viscosity-average molecular weight ($\overline{M}_v$) lies between $\overline{M}_n$ and $\overline{M}_w$ but closes to $\overline{M}_w$. Futhermore, in the special case of $\alpha = 1$ (from Mark-Houwink), $\overline{M}_v = \overline{M}_w$, but because $\alpha \neq 1$, $\overline{M}_v$ can never become identical to $\overline{M}_w$.

4.6 The Viscosity of Thickener

As stated earilier, the study of the effect of salt additions on the viscosity of polyacrylamide solutions, it is found that, the viscosity of polyacrylamide solutions was strongly influenced by the presence of sodium salt. Such effects are consequence of the ionic charges present on the polymer chains and in the case of anionic polyacrylamide, in the form of $R-CO-NH_2$. It is evident that the presence of salt significantly reduces the viscosity of the polymer solution (41).

The viscosity of thickener was studied as a function of concentration (6%, 8%, 10%, and 12% w/w) of starch and HSPAA in deionized distilled water. In the HSPAA system, the flow behavior in water depends predominantly on the gel fraction present. For thickening agents, the gel is

dispersed when water is added, the visco-elasticity occurs when the swollen gel particles are in an intimate contact. If the mixture is diluted (low concentration) to a level at which the swollen gel perticles are no longer in contact, being separated and then the mixture viscosity and elasticity decrease dramatically (55). It is evident that, the concentration of thickeners in distilled water (6%, 8%, 10%, and 12%) alters the viscosity at various shear rates, as shown in Tables 4.19-4.26 and the corresponding illustrations in Figures 4.26-4.33.

4.6.1 The effect of Gelatinized Cassava Starch Concentration on Viscosity

The viscosity profile aganist starch concentration is given in Table 4.19 and Figure 4.26, respectively. At a shear rate of 1 sec^{-1}, there is no difference in the viscosity profile from 6%, and 8% starch slurry concentrations. In the other shear rates, increasing the shear rate decreases the viscosity for every concentration of the solution. This property is known as shear-thinning or pseudoplasticity. The cassava starch can be used as thickener, but this material cannot be stored for a long time due to its biodegradability. For this reason, the starch graft copolymer is recommended because its stability is better than the starch paste (1).

Table 4.19

The Effect of Gelatinized Cassava Starch Concentration on Viscosity

Shear rate	log Viscosity (Pa.s)			
(sec^{-1})	6%	8%	10%	12%
1	0.39 $^{\otimes}$(2.5)	0.39 (2.5)	0.69 (5.0)	0.88 (7.5)
2	0.09 $^{\oplus}$(1.2)	0.39 (2.5)	0.57 (3.7)	0.69 (5.0)
4	-0.20 $^{\varnothing}$(0.6)	0.09 (1.2)	0.39 (2.5)	0.57 (3.7)
8	-0.50 ^{o}(0.3)	-0.30 (0.9)	0.27 (1.8)	0.49 (3.1)
20	-0.60 $^{\theta}$(0.2)	-0.12 (0.7)	0.14 (1.3)	0.39 (2.5)

(reading x factor x 10^{-3}, Pa.s) factors for shear rates of 1, 2, 4, 8, 20 sec^{-1} are 5,000, 2,500, 1,250, 625, 250. $\otimes$, $\oplus$, $\varnothing$, o, θ are the converting values, in Pa.s, from direct reading.

Figure 4.26   The effect of gelatinized cassava starch concentration on viscosity

4.6.2 The Effect of Molecular Weights of the Poly(sodium acrylate) on Viscosity Resulting from the Reaction Effect of Acrylic Acid

In this research, the starch-g-PAA was saponified with 25% NaOH solution, therefore, the ionic charges were bound on the grafted polymer chains (COO^-Na^+). Based on the previous work of Tam, K.C., and Tiu, C. (41), the effect of salt addition on the viscosity of anionic polymers was influenced by the presence of cations.

The viscosity experimental data from Table 4.20 show that the average molecular weights of HSPAA at 2.40M [AA] are less than the other acrylic acid concentrations. The smaller the molecular weight of the grafted polyacrylate, the smaller the sodium ion in the grafted chain of polyacrylate. According to Tam, K. C. et. al., (41) the viscosity increases with decreasing molecular weight of the hydrolyzed poly(acrylic acid).

Due to that the system was affected by shear rate, i.e., increasing the shear rate decreases the viscosity of the system, we can define the behavior as shear thinning or pseudoplasticity.

4.6.3 The Effect of Molecular Weights of the Poly(sodium acrylate) on Viscosity Resulting from the Reaction Effect of Hydrogen Peroxide

The apparent viscosity of HSPAA solutions were shown in Table 4.21 and Figure 4.28, respectively.

The molecular weights of HSPAA prepared by 3.86×10^{-1}M H_2O_2 was lower than the others. The grafted chains were short so the sodium salts in this copolymer were also decreased to cause the viscosity to increase.

Table 4.20

The Viscosity of HSPAA prepared by [H₂O₂] = 1.94x10⁻¹M, Starch = 60 g, Ascorbic acid = 0.33%, Temperature = 35°C, Time = 3 h, Addition rate = 0.0167 cm³/s, measured at 25°C by an RVT Brookfield Viscometer with A#14 spindle

Shear rate (sec⁻¹)	log Viscosity (Pa.s)															
	AA =1.70M[a]				AA = 2.06M[b]				AA = 2.40M[c]				AA = 2.73M[d]			
	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%
1	0.40 (2.5)	0.40 (2.5)	0.40 (2.5)	0.69 (5.0)	0.40 (2.5)	1.30 (20.0)	1.44 (27.5)	1.74 (55.0)	1.18 (15.0)	1.58 (30.0)	1.74 (55.0)	1.83 (67.5)	0.40 (2.5)	1.00 (10.0)	1.18 (15.0)	1.51 (32.5)
2	0.10 (1.2)	0.10 (1.2)	0.10 (1.2)	0.57 (3.7)	0.10 (1.2)	1.05 (11.2)	1.14 (13.7)	1.46 (28.7)	0.94 (8.7)	1.24 (17.5)	1.63 (42.5)	1.89 (77.5)	0.10 (1.2)	0.69 (5.0)	0.94 (8.7)	1.30 (20.0)
4	-0.20 (0.6)	-0.20 (0.6)	0.10 (1.2)	0.49 (3.1)	0.09 (1.2)	0.84 (6.8)	0.97 (9.3)	1.19 (15.6)	0.79 (6.2)	1.09 (12.5)	1.43 (26.8)	1.68 (47.5)	-0.20 (0.6)	0.57 (3.7)	0.79 (6.2)	1.14 (13.7)
8	-0.20 (0.6)	-0.03 (0.9)	0.19 (1.5)	0.40 (2.5)	-0.12 (0.9)	0.69 (5.0)	0.75 (5.6)	1.05 (11.2)	0.77 (5.9)	1.03 (10.6)	1.18 (15.0)	1.45 (28.1)	-0.20 (0.3)	0.33 (2.1)	0.64 (4.3)	0.93 (8.4)
20	-0.42 (0.3)	-0.30 (0.5)	0.00 (1.0)	0.18 (1.5)	-0.30 (0.5)	0.42 (2.6)	0.51 (3.2)	0.79 (6.2)	0.49 (3.1)	0.74 (5.5)	0.94 (8.6)	1.15 (14.2)	-0.20 (0.6)	0.18 (1.5)	0.43 (2.7)	0.69 (5.0)

[a]$\overline{M}_w$ = 583,262, [b]$\overline{M}_w$ = 543,338, [c]$\overline{M}_w$ = 525,767, [d]$\overline{M}_w$ = 651,967, (reading x factor x 10⁻³, Pa.s) factors for shear rates of 1, 2, 4, 8, 20 sec⁻¹ are 5,000, 2,500, 1,250, 625, 250. ⊗, ⊕, ∅, o, θ are the converting values, in Pa.s, from direct reading.
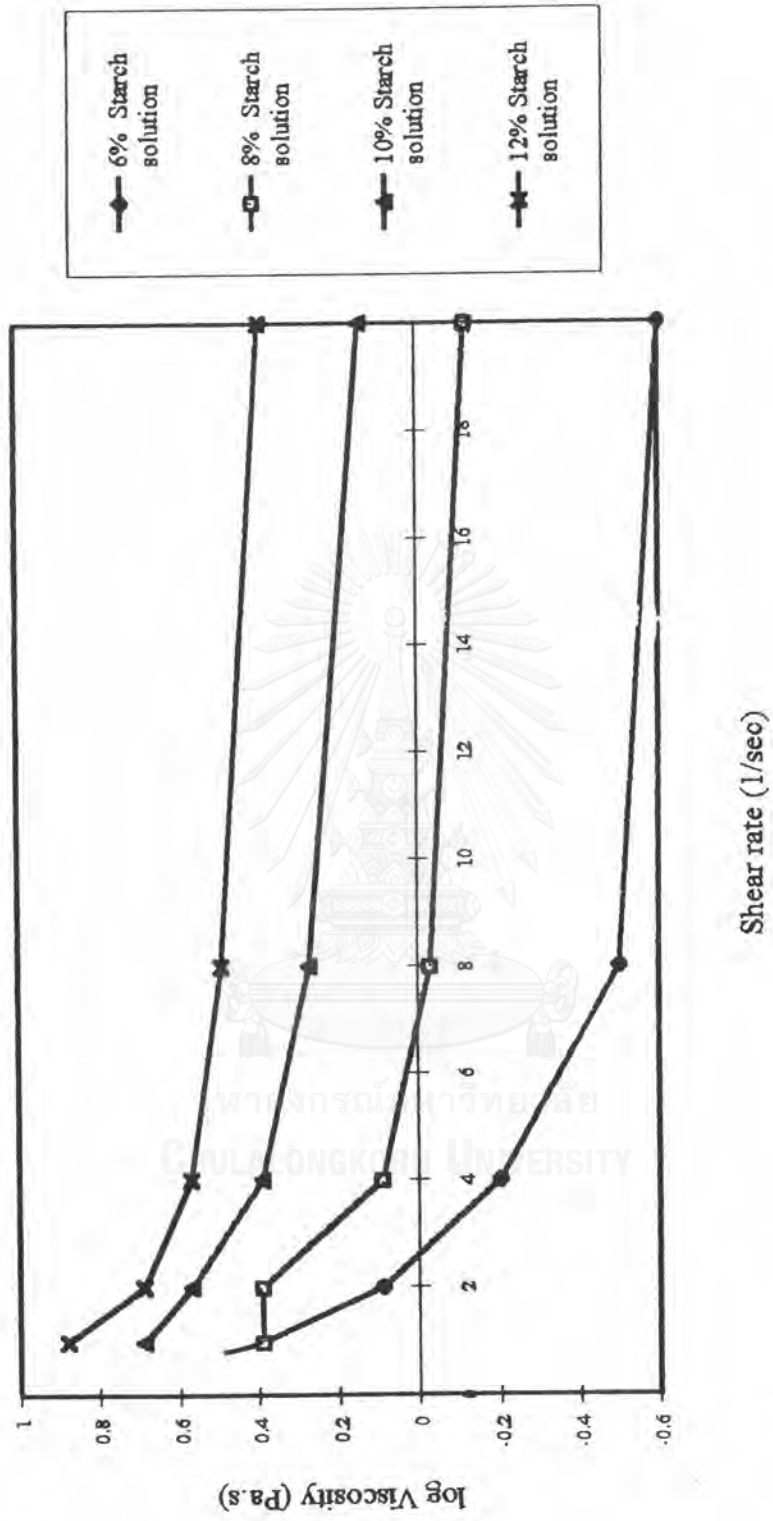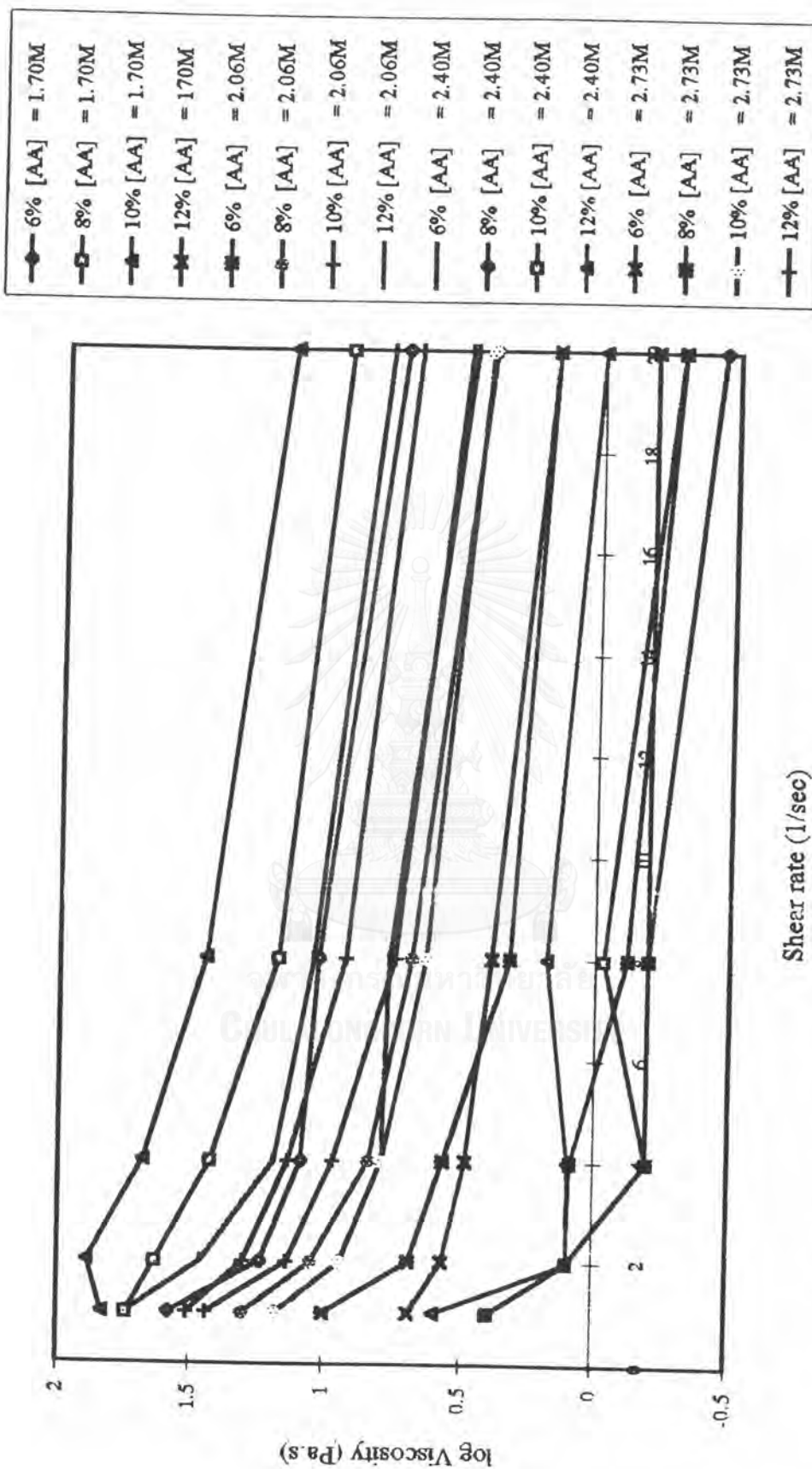
Figure 4.27   The effect of molecular weights of the poly(sodium acrylate) on viscosity resulting

from the reaction effect of acrylic acid

Table 4.21

The Viscosity of HSPAA prepared by [AA] = 1.70M, Starch = 60 g, Ascorbic acid = 0.33%, Temperature = 35°C, Time = 3 h, Addition rate = 0.0167 cm³/s, measured at 25°C by an RVT Brookfield Viscometer with A#14 spindle

Shear rate (sec⁻¹)	$H_2O_2 = 9.7 \times 10^{-2} M^a$				$H_2O_2 = 1.94 \times 10^{-1} M^b$				$H_2O_2 = 2.90 \times 10^{-1} M^c$				$H_2O_2 = 3.86 \times 10^{-1} M^d$			
	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%
1	0.69	0.87	1.54	1.69	0.40	0.40	0.40	0.69	0.87	1.09	1.51	1.72	1.63	1.63	1.79	2.13
	⊗(5.0)	(7.5)	(37.5)	(50.0)	(2.5)	(2.5)	(2.5)	(5.0)	(7.5)	(12.5)	(32.5)	(52.5)	(42.5)	(42.5)	(62.5)	(135)
2	0.57	0.79	1.39	1.46	0.10	0.10	0.10	0.57	0.69	0.94	1.30	1.57	1.39	1.42	1.54	1.86
	⊕(3.7)	(6.2)	(25.0)	(28.7)	(1.2)	(1.2)	(1.2)	(3.7)	(5.0)	(8.7)	(20.0)	(37.5)	(25.0)	(26.2)	(35.0)	(72.5)
4	0.40	0.69	1.30	1.24	-0.20	-0.20	0.10	0.49	0.47	0.69	1.07	1.36	1.21	1.23	1.27	1.61
	⊘(2.5)	(5.0)	(20.0)	(17.5)	(0.6)	(0.6)	(1.2)	(3.1)	(3.1)	(5.0)	(11.8)	(23.1)	(16.2)	(16.8)	(18.7)	(40.6)
8	0.27	0.69	1.06	1.13	-0.20	-0.03	0.19	0.40	0.34	0.57	0.87	1.18	1.04	1.05	1.06	1.43
	°(1.8)	(5.0)	(11.5)	(13.4)	(0.6)	(0.9)	(1.5)	(2.5)	(2.1)	(3.7)	(7.5)	(15.3)	(10.9)	(11.2)	(11.5)	(16.8)
20	0.05	0.46	0.78	0.87	-0.42	-0.30	0.00	0.18	0.09	0.30	0.58	0.90	0.79	0.83	0.84	1.21
	θ(1.1)	(2.8)	(6.0)	(7.3)	(0.3)	(0.5)	(1.0)	(1.5)	(1.2)	(0.2)	(3.8)	(8.0)	(6.0)	(6.7)	(6.8)	(16.1)

log Viscosity (Pa.s)

$^a\bar{M}_w = 372,654$, $^b\bar{M}_w = 583,262$, $^c\bar{M}_w = 369,813$, $^d\bar{M}_w = 269,099$, (reading x factor x 10^{-3}, Pa.s) factors for shear rates of 1, 2, 4, 8, 20 sec⁻¹ are 5,000, 2,500, 1,250, 625, 250. ⊗, ⊕, ⊘, o, θ are the converting values, in Pa.s, from direct reading.
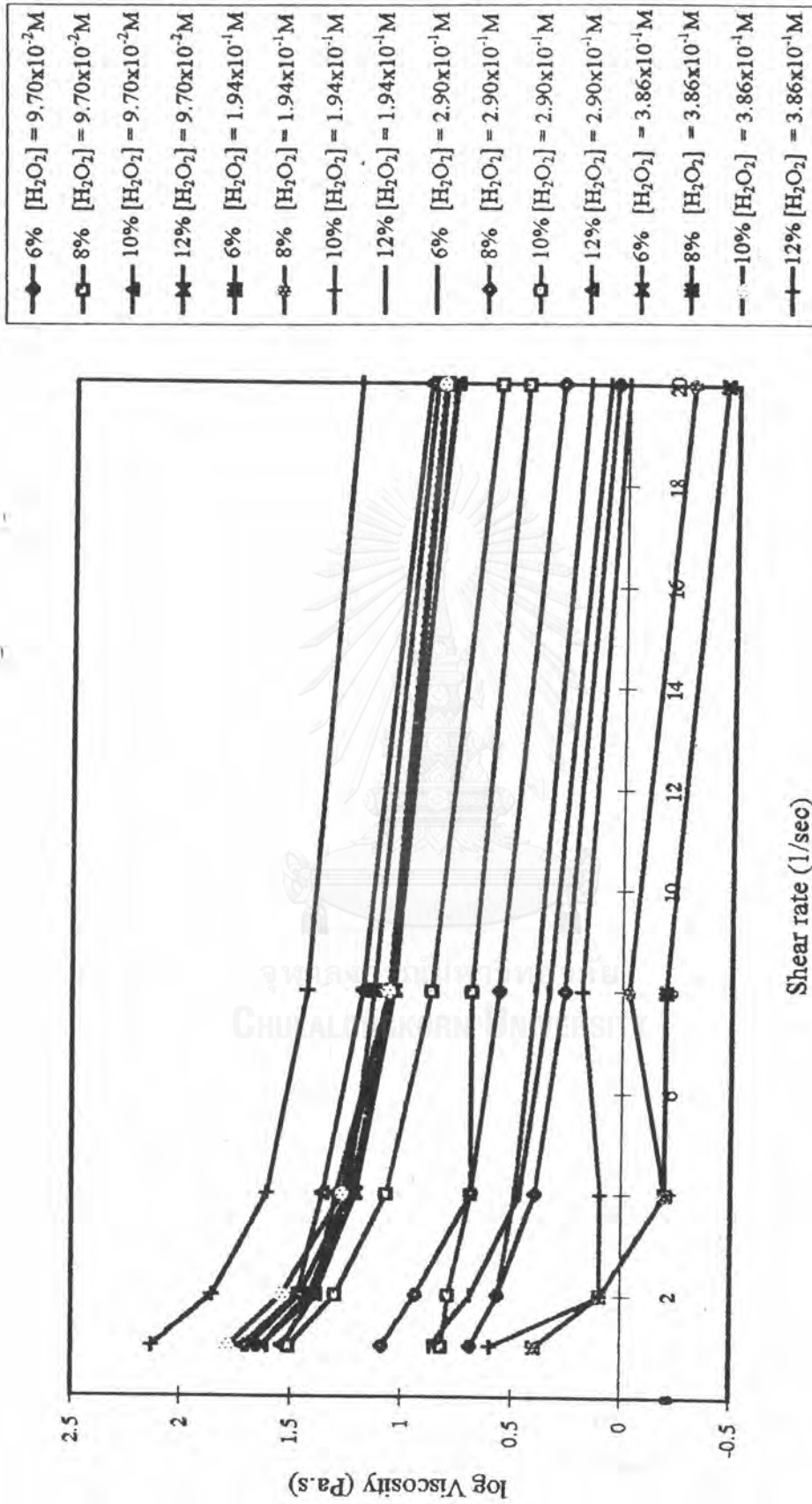
Figure 4.28   The effect of molecular weights of the poly(sodium acrylate) on viscosity resulting

from the reaction effect of hydrogen peroxide

4.6.4 <u>The Effect of Molecular Weights of the Poly(sodium acrylate) on Viscosity Resulting from the Reaction Effect of Starch</u>

The apparent viscosity of HSPAA solutions was shown in Table 4.22 and Figure 4.29 , respectively.

The molecular weight of HSPAA prepared by starch 50g was smaller than the others. The grafted chains were short, so the sodium salts in this sample were also decreased. In the case of 60, 70 and 80 g starch, increasing the grafted chains decreases the amount of sodium salts on the polymer chains. It is evident that increasing in ionic character of the polymer decreased the viscosity (41).

4.6.5 <u>The Effect of Molecular Weights of the Poly(sodium acrylate) on Viscosity Resulting from the Reaction Effect of Ascorbic Acid</u>

The viscosity experimental data in Table 4.23 and Figure 4.30 show that the average molecular weight of the HSPAA, prepared by ascorbic acid 0.67%wt of 231,539, is the lowest molecular weight. The viscosity of this sample was higher than those prepared by other ascorbic acid concentrations. The sodium salts in the grafted polymer chains decreased to cause the viscosity to increase. In other words, the molecular weights of the solution increases when the viscosity is decreased.

4.6.6 <u>The Effect of Molecular Weights of the Poly(sodium acrylate) on Viscosity Resulting from the Reaction Effect of Reaction Temperature</u>

In Table 4.24 and Figure 4.31, the viscosity experimental data show that the HSPAA prepared by various reaction temperatures, gave the average molecular weights range from 239,731, 238,838, 583,262, and 480,377

Table 4.22

The Viscosity of HSPAA prepared by [AA] = 1.70M, $[H_2O_2]$ = 1.94x10^{-1}M, Ascorbic acid = 0.33%, Temperature = 35°C, Time = 3 h, Addition rate = 0.0167 cm³/s, measured at 25°C by an RVT Brookfield Viscometer with A#14 spindle

Shear rate (sec^{-1})	log Viscosity (Pa.s)															
	Starch = 50 g^a				Starch = 60 g^b				Starch = 70 g^c				Starch = 80 g^d			
	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%
1	1.24 ⊗(17.5)	1.30 (20.0)	1.81 (65.0)	2.54 (345)	0.40 (2.5)	0.40 (2.5)	0.40 (2.5)	0.69 (5.0)	0.40 (2.5)	0.40 (2.5)	0.88 (7.5)	1.09 (12.)	0.40 (2.5)	1.09 (12.5)	1.18 (15.0)	1.72 (52.5)
2	1.09 ⊕(12.5)	1.05 (11.2)	1.49 (31.2)	2.25 (178)	0.10 (1.2)	0.10 (1.2)	0.10 (1.2)	0.57 (3.7)	0.10 (1.2)	0.10 (1.2)	0.69 (5.0)	0.94 (8.7)	0.40 (2.5)	1.00 (8.7)	1.00 (10.0)	1.51 (32.5)
4	0.91 ⊘(8.1)	0.92 (6.2)	1.23 (16.8)	1.96 (91.8)	-0.20 (0.6)	-0.20 (0.6)	0.10 (1.2)	0.49 (3.1)	-0.20 (0.6)	0.10 (1.2)	0.58 (3.7)	0.79 (6.2)	0.27 (1.8)	0.69 (5.0)	0.75 (5.6)	1.27 (18.7)
8	0.75 °(5.6)	0.54 (3.4)	0.89 (9.6)	1.69 (49.0)	-0.20 (0.6)	-0.03 (0.9)	0.19 (1.5)	0.40 (2.5)	-0.20 (0.6)	0.10 (1.2)	0.45 (2.8)	0.64 (4.3)	0.09 (1.2)	0.54 (3.4)	0.54 (3.4)	1.06 (11.5)
20	0.60 θ(4.0)	0.27 (1.8)	0.71 (5.1)	1.38 (24.2)	-0.42 (0.3)	-0.30 (0.5)	0.00 (1.0)	0.18 (1.5)	-0.42 (0.3)	-0.12 (0.7)	0.24 (1.7)	0.46 (2.8)	-0.20 (0.6)	0.27 (1.8)	0.30 (2.0)	0.77 (5.8)

$^a\overline{M}_w$ = 509,498, $^b\overline{M}_w$ = 583,262, $^c\overline{M}_w$ = 523,306, $^d\overline{M}_w$ = 517,270, (reading x factor x 10^{-3}, Pa.s) factors for shear rates of 1, 2, 4, 8, 20 sec^{-1} are 5,000, 2,500, 1,250, 625, 250. ⊗, ⊕, ∅, o, θ are the converting values, in Pa.s, from direct reading.
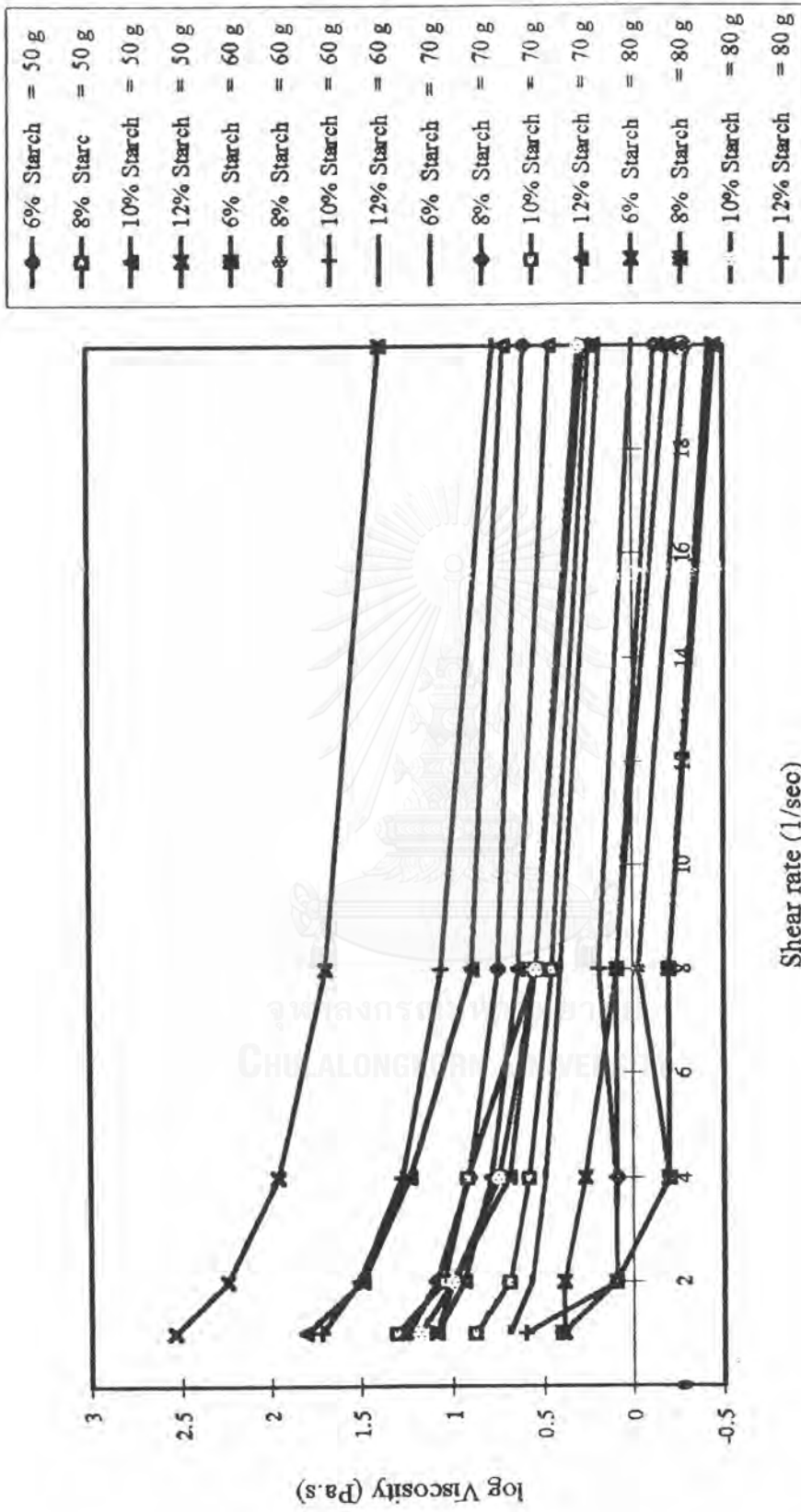
Figure 4.29   The effect of molecular weights of the poly(sodium acrylate) on viscosity resulting

from the reaction effect of starch

Table 4.23

The Viscosity of HSPAA prepared by [AA] = 1.70M, [H_2O_2] = 1.94×10^{-1}M, Starch = 60 g, Temperature = 35°C,

Time = 3 h, Addition rate = 0.0167 cm³/s, measured at 25 °C by an RVT Brookfield Viscometer with A#14 spindle

Shear rate (sec⁻¹)	Ascorbic acid = 0.16%[a]				Ascorbic acid = 0.33%[b]				Ascorbic acid = 0.50%[c]				Ascorbic acid = 0.67%[d]			
	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%
1	0.40	1.00	1.30	1.57	0.40	0.40	0.40	0.69	1.09	1.63	1.72	1.89	1.18	1.60	1.84	2.16
	⊗(2.5)	(10.0)	(20.0)	(37.5)	(2.5)	(2.5)	(2.5)	(5.0)	(12.5)	(22.5)	(52.5)	(77.5)	(15.0)	(40.0)	(70.0)	(145)
2	0.10	0.79	1.14	1.39	0.10	0.10	0.10	0.57	0.88	1.14	1.14	1.62	0.94	1.38	1.64	1.95
	⊕(1.2)	(6.2)	(13.7)	(25.0)	(1.2)	(1.2)	(1.2)	(3.7)	(7.5)	(13.7)	(37.5)	(41.2)	(8.7)	(23.7)	(43.7)	(90.0)
4	0.10	0.64	0.94	1.21	-0.20	-0.20	0.10	0.49	0.69	0.91	0.91	1.35	0.75	1.19	1.45	1.74
	⌀(1.2)	(4.3)	(8.7)	(16.2)	(0.6)	(0.6)	(1.2)	(3.1)	(5.0)	(8.1)	(24.3)	(22.5)	(5.6)	(15.6)	(28.1)	(54.3)
8	-0.20	0.45	0.75	1.01	-0.20	-0.03	0.19	0.40	0.49	0.69	0.69	1.19	0.57	0.97	1.26	1.55
	°(0.6)	(2.8)	(5.6)	(10.3)	(0.6)	(0.9)	(1.5)	(2.5)	(3.1)	(5.0)	(15.6)	(15.3)	(3.7)	(9.3)	(18.1)	(35.6)
20	-0.43	0.21	0.53	0.77	-0.42	-0.30	0.00	0.18	0.21	0.42	0.94	1.01	0.30	0.73	0.99	1.32
	ϴ(0.3)	(1.6)	(3.3)	(5.8)	(0.3)	(0.5)	(1.0)	(1.5)	(1.6)	(2.6)	(8.7)	(10.1)	(2.0)	(5.3)	(9.8)	(21.1)

[a]$\bar{M}_w$ = 495,714, [b]$\bar{M}_w$ = 583,262, [c]$\bar{M}_w$ = 516,135, [d]$\bar{M}_w$ = 231,539, (reading x factor x 10^{-3}, Pa.s) factors for shear rates of 1, 2, 4, 8, 20

sec⁻¹ are 5,000, 2,500, 1,250, 625, 250. ⊗, ⊕, ⌀, o, ϴ are the converting values, in Pa.s, from direct reading.
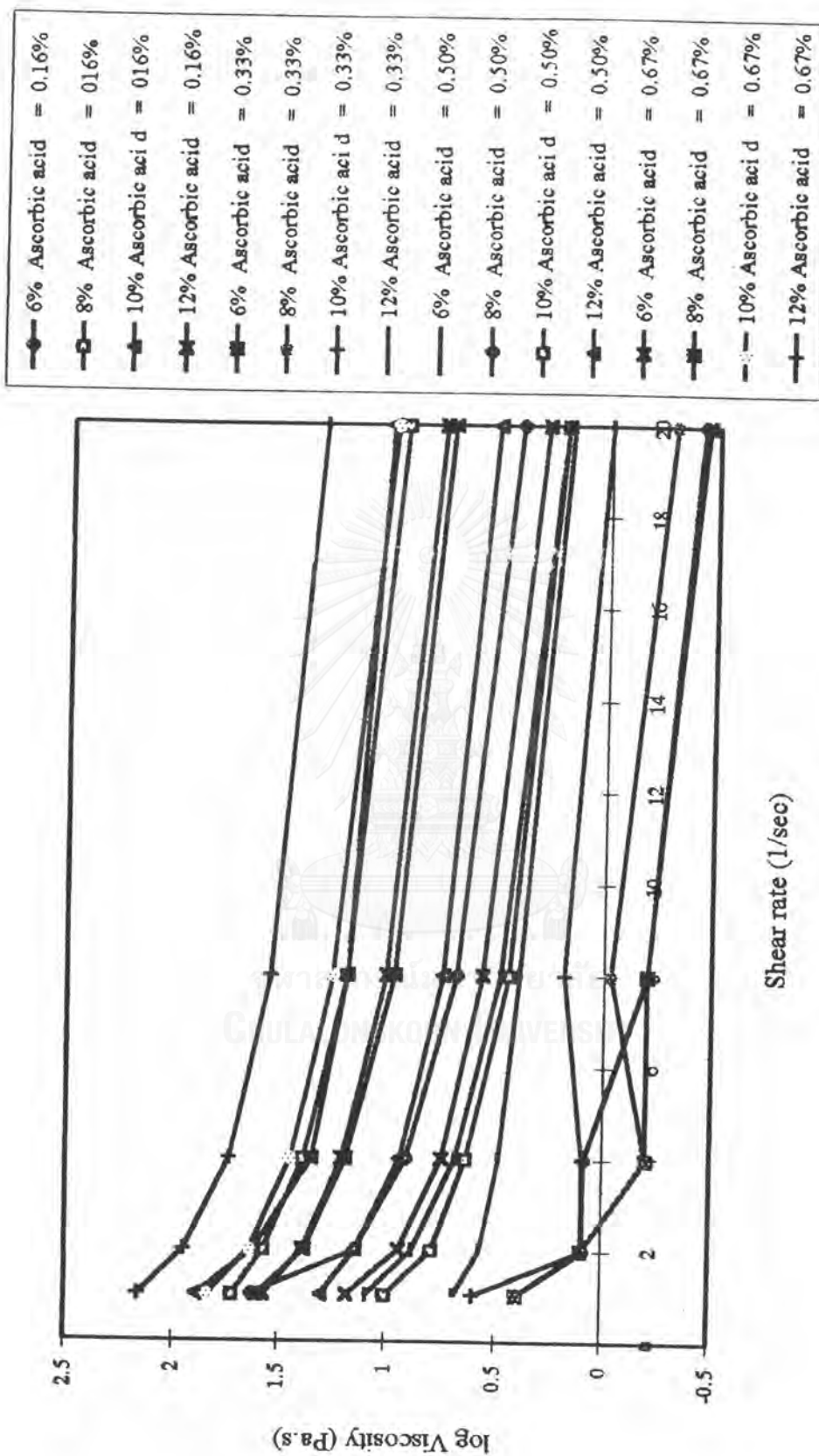
Figure 4.30 The effect of molecular weights of the poly(sodium acrylate) on viscosity resulting from the reaction effect of ascorbic acid

Table 4.24

The Viscosity of HSPAA prepared by [AA] = 1.70M, [H$_2$O$_2$] = 1.94X10^{-1}M, Starch = 60 g, Ascorbic acid = 0.33%,

Time = 3 h, Addition rate = 0.0167 cm^3/s, measured at 25°C by an RVT Brookfield Viscometer with A#14 spindle

Shear rate (sec^{-1})	Temperature = 25°C[a]				Temperature = 30°C[b]				Temperature = 35°C[c]				Temperature = 40°C[d]			
	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%
1	0.88 (⊗7.5)	1.24 (17.5)	1.54 (37.5)	1.72 (52.5)	1.24 (17.5)	1.57 (37.5)	1.93 (85.0)	2.21 (162)	0.40 (2.5)	0.40 (2.5)	0.40 (2.5)	0.69 (5.0)	0.40 (2.5)	0.40 (2.5)	0.69 (5.0)	0.88 (7.5)
2	0.69 (⊕5.0)	1.05 (11.2)	1.30 (20.0)	1.49 (31.2)	1.05 (11.2)	1.38 (23.7)	1.71 (51.2)	1.92 (83.7)	0.10 (1.2)	0.10 (1.2)	0.10 (1.2)	0.57 (3.7)	0.10 (1.2)	0.10 (1.2)	0.57 (3.7)	0.69 (5.0)
4	0.49 (⊘3.1)	0.88 (7.5)	1.16 (14.3)	1.26 (18.1)	0.84 (6.8)	1.18 (15.0)	1.47 (29.3)	1.69 (50.0)	-0.20 (0.6)	-0.20 (0.6)	0.10 (1.2)	0.49 (3.1)	-0.20 (0.6)	0.10 (1.2)	0.39 (2.50)	0.57 (3.7)
8	0.27 (°1.8)	0.67 (4.6)	1.01 (10.3)	1.09 (12.1)	0.64 (4.3)	1.00 (10.0)	1.24 (17.5)	1.45 (28.4)	-0.20 (0.6)	-0.03 (0.9)	0.19 (1.5)	0.40 (2.5)	-0.50 (0.3)	-0.20 (0.6)	0.19 (1.5)	0.34 (2.1)
20	0.00 (θ1.0)	0.42 (2.6)	0.79 (6.0)	0.98 (9.7)	0.42 (2.6)	0.78 (6.0)	1.04 (11.0)	1.23 (16.8)	-0.42 (0.3)	-0.30 (0.5)	0.00 (1.0)	0.18 (1.5)	-0.60 (0.2)	-0.50 (0.3)	0.00 (1.0)	0.14 (1.3)

[a]$\overline{M}_w$ = 239,731, [b]$\overline{M}_w$ = 238,838, [c]$\overline{M}_w$ = 583,262, [d]$\overline{M}_w$ = 480,377, (reading x factor x 10^{-3}, Pa.s) factors for shear rates of 1, 2, 4, 8, 20

sec^{-1} are 5,000, 2,500, 1,250, 625, 250. ⊗, ⊕, Ø, o, θ are the converting values, in Pa.s, from direct reading.
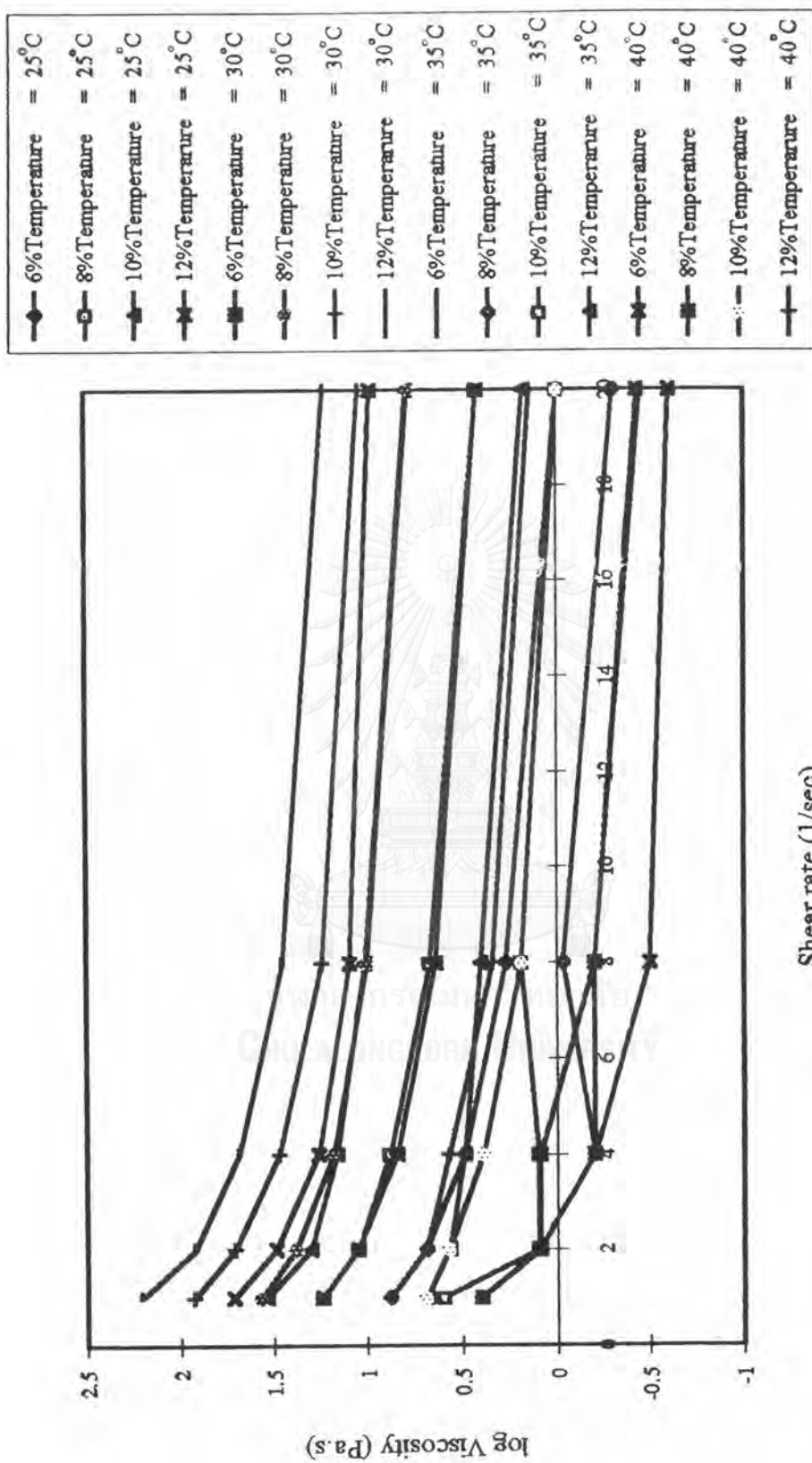
Figure 4.31 The effect of molecular weights of the poly(sodium acrylate) on viscosity resulting

from the reaction effect of reaction temperature

by the reaction temperatures at 25, 30, 35, and 40°C, respectively. As a result, the viscosity was effected by the sodium salts bound on the length of the grafted polyacrylate. By increasing the sodium salt, the viscosity was decreased. At all reaction temperatures, the solution shows a shear-thinning behavior. This means, for every concentration of the solution, the viscosity decreases when the shear rate increased.

4.6.7 The Effect of Molecular Weights of the Poly(sodium acrylate) on Viscosity Resulting from the Reaction Effect of Reaction Time

The viscosity data from the experiment is tabulated in Table 4.25 and shown in Figure 4.32, respectively.

The graft copolymers prepared at reaction times 2, 3, 4, and 5 h, gave the decreasing viscosity with shear rate. All solutions display a non-Newtonian behavior. The graft copolymer with higher average molecular weights increases the content of the sodium salt and therefore the viscosity decreases accordingly due to salt effect.

4.6.8 The Effect of Molecular Weights of the Poly(sodium acrylate) on Viscosity Resulting from the Reaction Effect of the Addition Rate of Monomer-Initiator Mixture

The experimental data in Table 4.26 and Figure 4.33 show that the viscosity of the graft copolymer prepared by the addition rate of H_2O_2-acrylic acid mixture at 0.0167 cm^3/s produces the lowest value. The extent of viscosity values depends on molecular weights of the hydrolyzed cassava starch graft poly(acrylic acid). As a result, the sodium salts in the graft copolymer are therefore increased. The longer grafted chain of sodium salt strongly influences the viscosity than those of the short grafted chains.

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Table 4.25

The Viscosity of HSPAA prepared by [AA] = 1.70M, [H$_2$O$_2$] = 1.94X10^{-1} M, Starch = 60 g, Ascorbic acid = 0.33%,

Temperature = 35°C, Addition rate = 0.0167 cm^3/s, measured at 25°C by an RVT Brookfield Viscometer with A#14 spindle

Shear rate (sec^{-1})	log Viscosity (Pa.s)															
	Time = 2 h[a]				Time = 3 h[b]				Time = 4 h[c]				Time = 5 h[d]			
	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%
1	0.69	1.05	1.79	1.85	0.40	0.40	0.40	0.69	0.69	1.51	1.76	2.15	0.40	0.40	0.69	1.09
	(5.0)	(12.5)	(62.5)	(70.0)	(2.5)	(2.5)	(2.5)	(5.0)	(5.0)	(32.5)	(57.5)	(140)	(2.5)	(2.5)	(5.0)	(12.5)
2	0.57	0.94	1.56	1.59	0.10	0.10	0.10	0.57	0.57	1.27	1.48	1.82	0.10	0.10	0.57	0.88
	(3.7)	(8.7)	(36.2)	(40.0)	(1.2)	(1.2)	(1.2)	(3.7)	(3.7)	(17.5)	(30.0)	(71.2)	(1.2)	(1.2)	(3.7)	(7.5)
4	0.39	0.64	1.36	1.39	-0.20	-0.20	0.10	0.49	0.49	0.97	1.23	1.55	-0.20	-0.10	0.40	0.69
	(2.5)	(4.3)	(23.1)	(2.50)	(0.6)	(0.6)	(1.2)	(3.1)	(3.1)	(9.3)	(16.8)	(35.6)	(0.6)	(1.2)	(2.5)	(5.0)
8	0.27	0.45	1.21	1.18	-0.20	-0.03	0.19	0.40	0.27	0.69	0.99	1.30	-0.50	-0.30	0.19	0.49
	(1.8)	(2.8)	(15.9)	(15.0)	(0.6)	(0.9)	(1.5)	(2.5)	(1.8)	(5.0)	(9.6)	(20.0)	(0.3)	(0.9)	(1.5)	(3.1)
20	0.00	0.24	0.97	0.98	-0.42	-0.30	0.00	0.18	0.09	0.39	0.71	1.01	-0.60	-0.30	-0.60	0.24
	(1.0)	(1.7)	(9.2)	(9.5)	(0.3)	(0.5)	(1.0)	(1.5)	(1.2)	(2.5)	(5.1)	(10.2)	(0.2)	(0.5)	(0.8)	(1.7)

[a]$\overline{M}_w$ = 497,003, [b]$\overline{M}_w$ = 583,262, [c]$\overline{M}_w$ = 376,937, [d]$\overline{M}_w$ = 508,912, (reading x factor x 10^{-3}, Pa.s) factors for shear rates of 1, 2, 4, 8, 20 sec^{-1} are 5,000, 2,500, 1,250, 625, 250. ⊗, ⊕, ∅, o, θ are the converting values, in Pa.s, from direct reading.
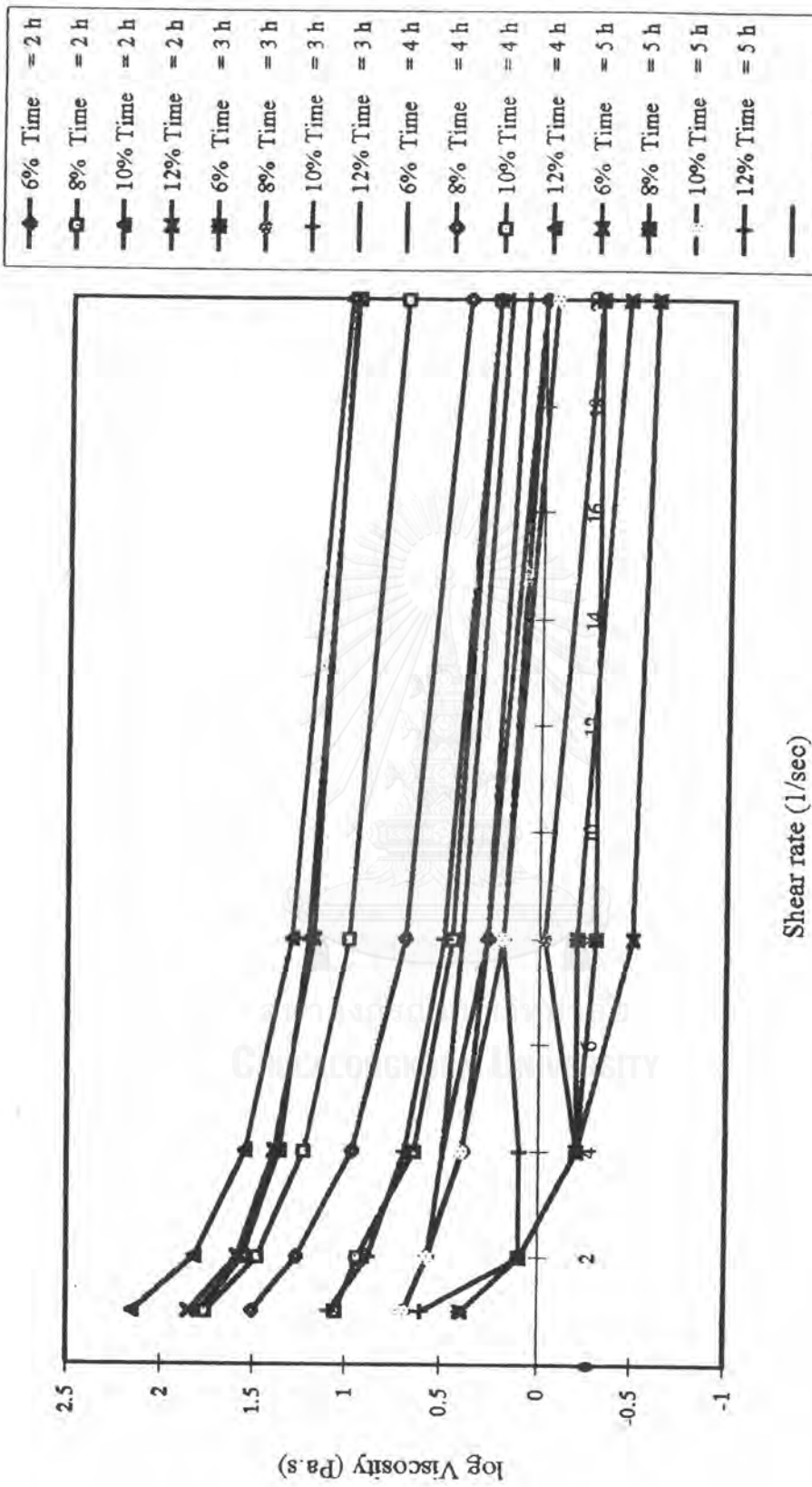
Figure 4.32   The effect of molecular weights of the poly(sodium acrylate) on viscosity resulting

from the reaction effect of reaction time

Table 4.26

The Viscosity of HSPAA prepared by [AA] = 1.70M, [H_2O_2] = 1.94X10⁻¹M, Starch = 60 g, Ascorbic acid = 0.33%,

Temperature = 35°C, Time = 3 h, measured at 25°C by an RVT Brookfield Viscometer with A#14 spindle

Shear rate (sec⁻¹)	log Viscosity (Pa.s)															
	Addition rate = 0.0167 cm³/s [a]				Addition rate = 0.0250 cm³/s [b]				Addition rate = 0.0333 cm³/s [c]				Addition rate = 0.0417 cm³/s [d]			
	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%	6%	8%	10%	12%
1	0.40 ⊗	0.40	0.40	0.69	0.40	0.40	0.69	0.88	0.69	0.88	1.09	1.25	0.40	0.69	0.88	1.30
	(2.5)	(2.5)	(2.5)	(5.0)	(2.5)	(2.5)	(5.0)	(7.5)	(5.0)	(7.5)	(12.5)	(22.5)	(2.5)	(5.0)	(7.5)	(20.0)
2	0.10 ⊕	0.10	0.10	0.57	0.60	0.09	0.57	0.69	0.40	0.69	0.87	1.14	0.40	0.57	0.69	1.09
	(1.2)	(1.2)	(1.2)	(3.7)	(1.2)	(1.2)	(3.7)	(5.0)	(2.5)	(5.0)	(7.5)	(13.7)	(2.5)	(3.7)	(5.0)	(12.5)
4	-0.20 ⊘	-0.20	0.10	0.49	-0.20	0.09	0.39	0.49	0.27	0.49	0.69	0.94	0.10	0.39	0.49	0.09
	(0.6)	(0.6)	(1.2)	(3.1)	(0.6)	(1.2)	(2.5)	(3.1)	(1.8)	(3.1)	(5.0)	(8.7)	(0.1)	(2.5)	(3.1)	(8.1)
8	-0.20 °	-0.03	0.19	0.40	-0.51	-0.30	0.19	0.34	0.10	0.27	0.49	0.77	-0.03	0.27	0.27	0.73
	(0.6)	(0.9)	(1.5)	(2.5)	(0.3)	(0.9)	(1.5)	(2.1)	(1.2)	(1.8)	(3.1)	(5.9)	(0.9)	(1.8)	(1.8)	(5.3)
20	-0.42 θ	-0.30	0.00	0.18	-0.60	-0.30	0.00	0.18	-0.20	0.05	0.27	0.53	-0.30	0.00	0.00	0.51
	(0.3)	(0.5)	(1.0)	(1.5)	(0.2)	(0.5)	(1.0)	(1.5)	(0.6)	(1.1)	(1.8)	(3.3)	(0.5)	(1.0)	(1.0)	(3.2)

[a]$\overline{M}_w$ = 583,262, [b]$\overline{M}_w$ = 311,536, [c]$\overline{M}_w$ = 255,895, [d]$\overline{M}_w$ = 282,938, (reading x factor x 10⁻³, Pa.s) factors for shear rates of 1, 2, 4, 8, 20 sec⁻¹ are 5,000, 2,500, 1,250, 625, 250. ⊗, ⊕, ∅, o, θ are the converting values, in Pa.s, from direct reading.
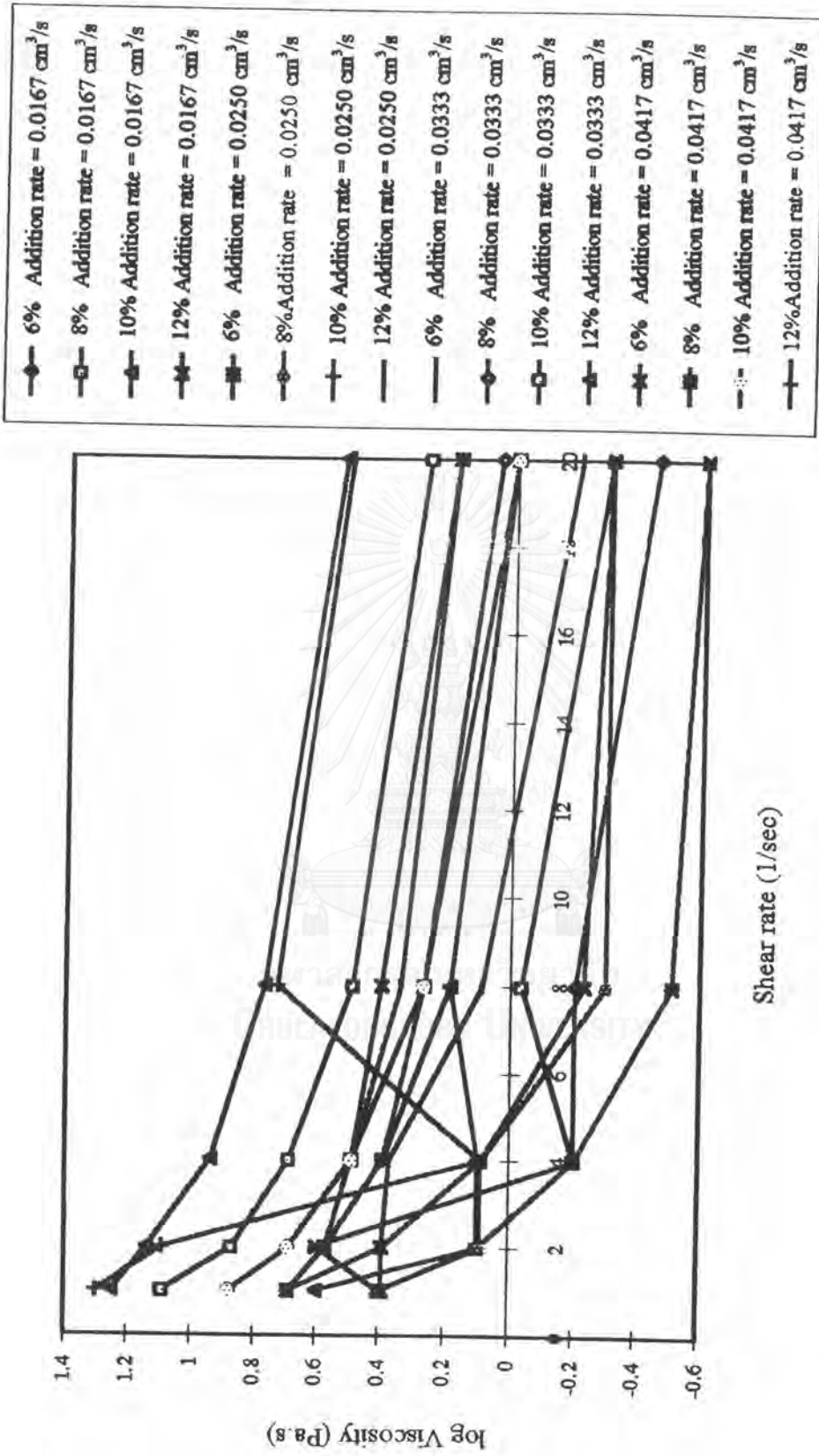
Figure 4.33 The effect of molecular weights of the poly(sodium acrylate) on viscosity resulting

from the reaction effect of addition rate of monomer-initiator mixture

4.7 The Viscosity of Sodium Alginate-700

The apprarent viscosity data of sodium alginate-700 solutions were shown in Table 4.27 and Figure 4.34, respectively.

Table 4.27

The Effect of Sodium Alginate Concentration on Viscosity

Shear rate	log Viscosity (Pa.s)			
(sec^{-1})	6%	8%	10%	12%
0.2	NA	NA	NA	2.67 $^{◊}$(462.5)
0.4	NA	NA	NA	2.51 *(325.0)
1	1.09 $^{⊗}$(12.5)	1.54 (35.0)	1.98 (95.0)	2.30 (200.0)
2	1.00 $^{⊕}$(10.0)	1.44 (27.5)	1.80 (72.5)	2.15 (142.5)
4	0.87 $^{⊘}$(5.9)	1.33 (21.2)	1.74 (55.0)	2.02 (104.3)
8	0.77 ^{o}(5.9)	1.22 (16.5)	1.60 (40.6)	NA
20	0.65 ^{θ}(4.5)	1.07 (11.6)	1.90 (25.0)	NA

(reading x factor x 10^{-3}, Pa.s), factors for shear rates of 1, 2, 4, 8, 20 sec^{-1} are 25,000, 12,500, 5,000, 2,500, 1,250, 625, 250. ◊, *, ⊗, ⊕, ⊘, o, θ are the converting values, in Pa.s, from direct reading, NA = not available.

From all viscosities experiment data (Tables 4.20-4.37) are indicate that the viscosity of sodium alginate is higher than hydrolyzed starch-g-polt(acrylic acid) at every concentration. The high viscosity, long chain are more sensitive to shear and have short flow characteristics. Conversely, the low viscosity, short chain are much more stable to shear and have long flow properties (55). In this research, the starch-g-PAA was saponified with 25% NaOH solution, the effect of sodium salt addition (Na^{+}) reduce the viscosity of
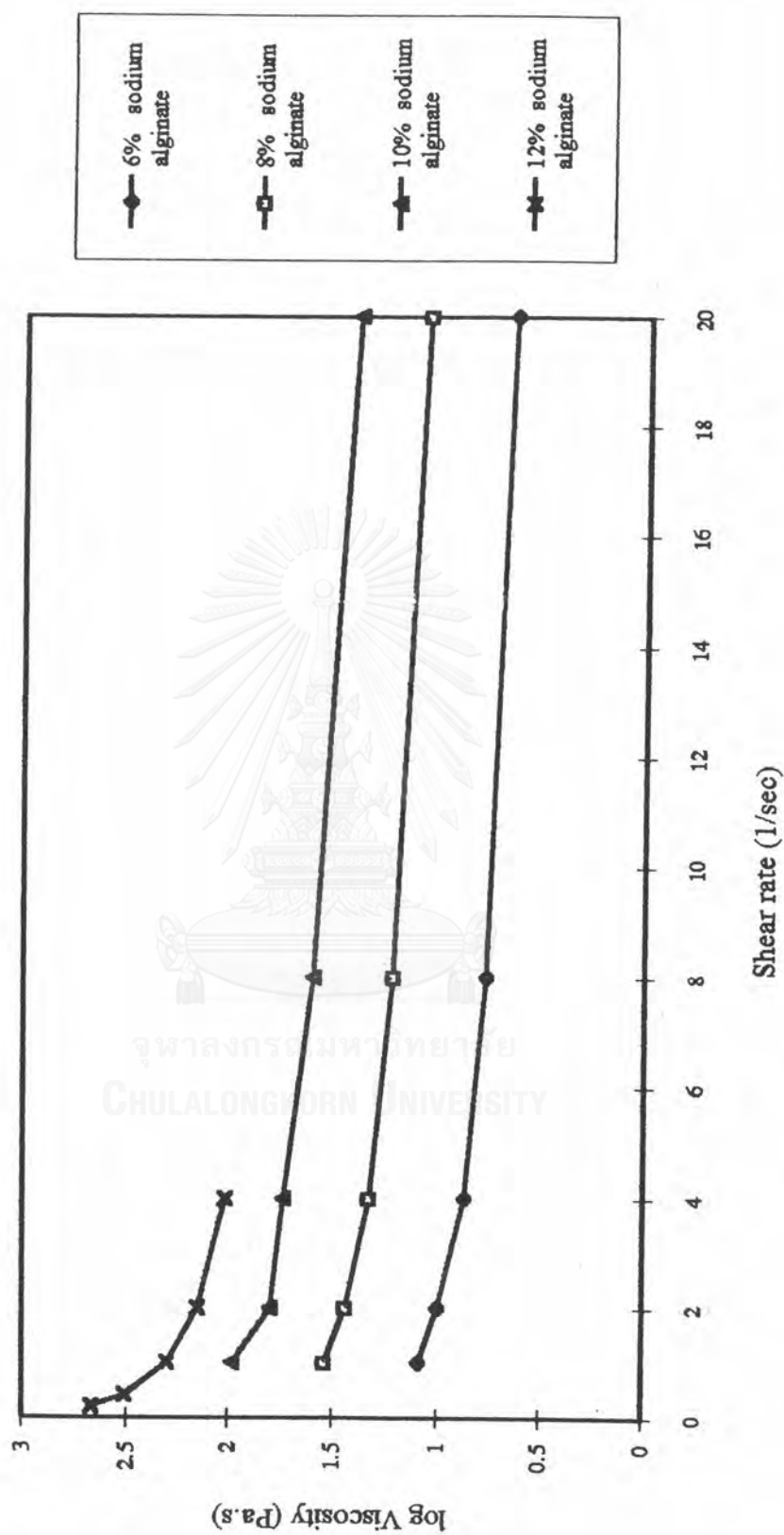
Figure 4.34   The effect of sodium alginate-700 concentration on viscosity

HSPAA solutions. Therefore the viscosity of HSPAA decreases higher than the sodium alginate because the grafted polymer chains contact as the ionic strength in medium increases.

To conclude, thickening will differ in their rheological properties from ideal viscous solutions as defined coils which is termed "structural viscosity". All the HSPAA and sodium alginate-700 solutions decrease in viscosity with increasing shear rates. This propertiy is known as *shear thinning or pseudoplasticity*. In good solvent, the thickener molecule is disentangled, stretched out that becomes a loose molecule. When the solution is at rest, the molecules will interfere with each other forming loose entanglements. When shear is applied to the solution, the molecules are oriented in the direction of the shearing force. The association between the molecule is greatly reduced and there are no longer any entanglements. The result is an immediate lowering of viscosity. When the shear is removed, the molecules entangle again, which results in the recovery of the original viscosity (55).