CHAPTER IV

RESULTS and DISCUSSION

Infrared Analyses

FT-IR technique was used to follow up changes in graft copolymerization. The FT-IR spectra of cassava starch, and the copolymers after grafting, after extraction, and after saponification are given in Table 4.1 and Figures 4.1 through 4.4, respectively.
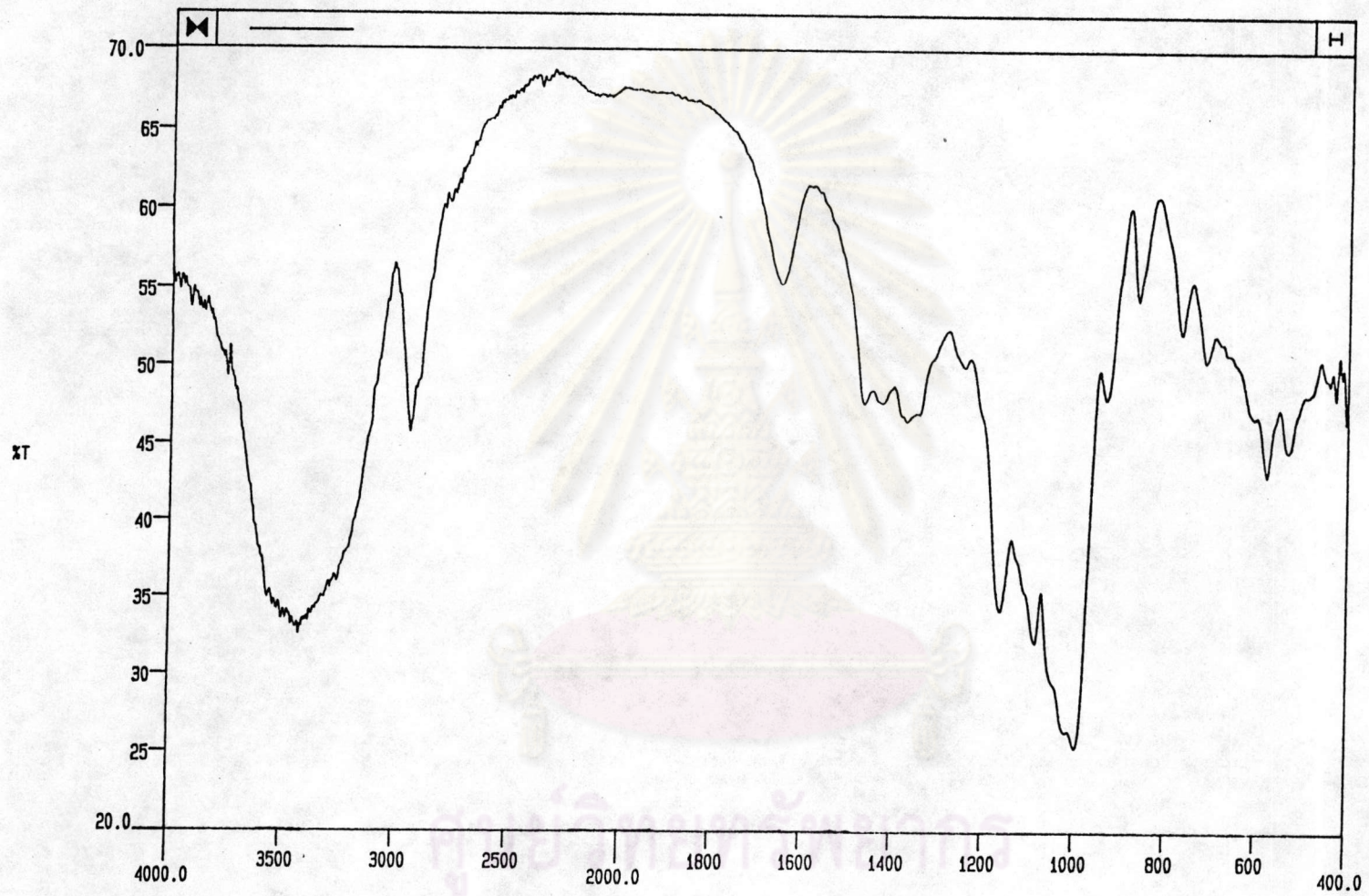
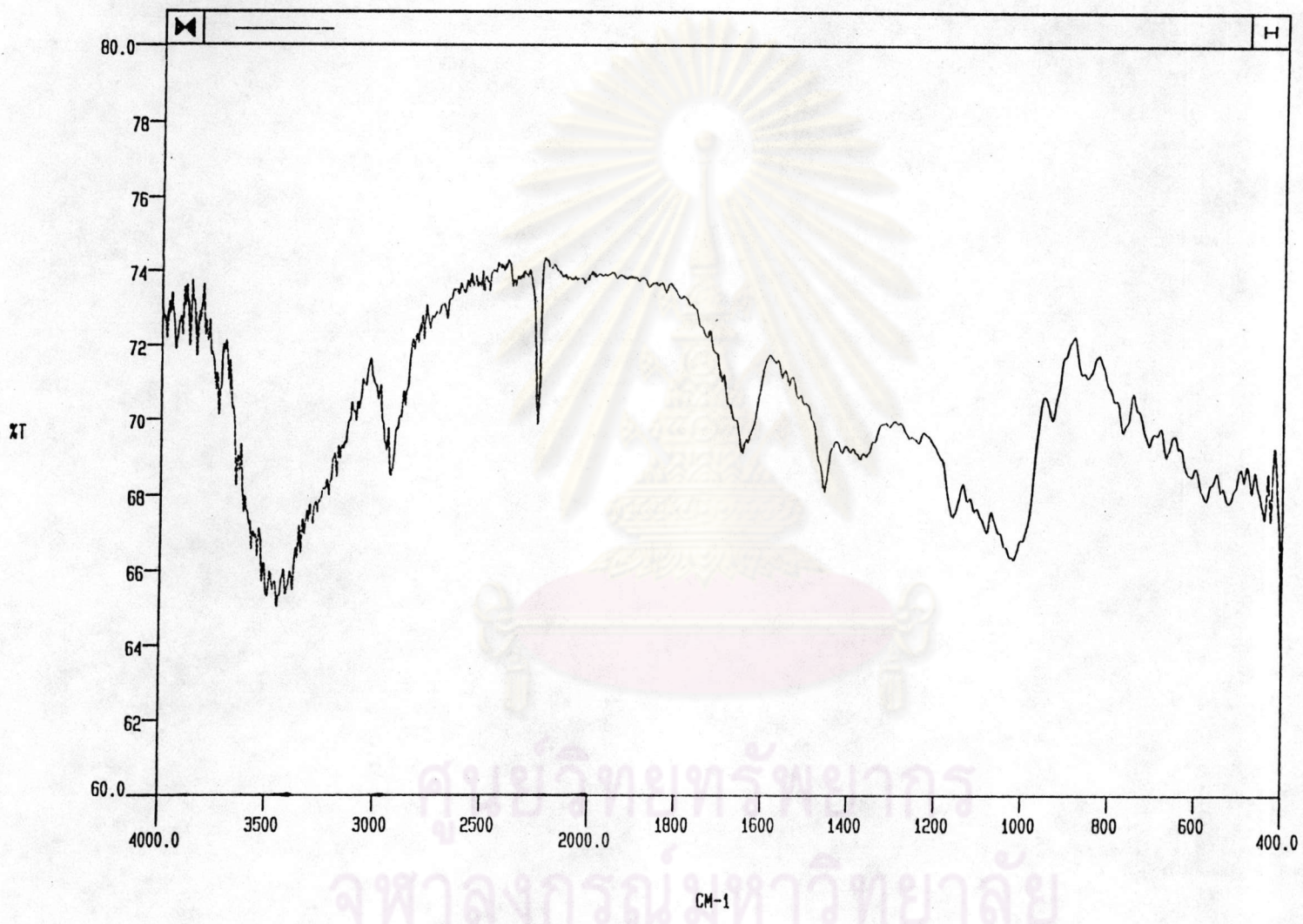Figure 4.1 Infrared spectrum of dried cassava starch

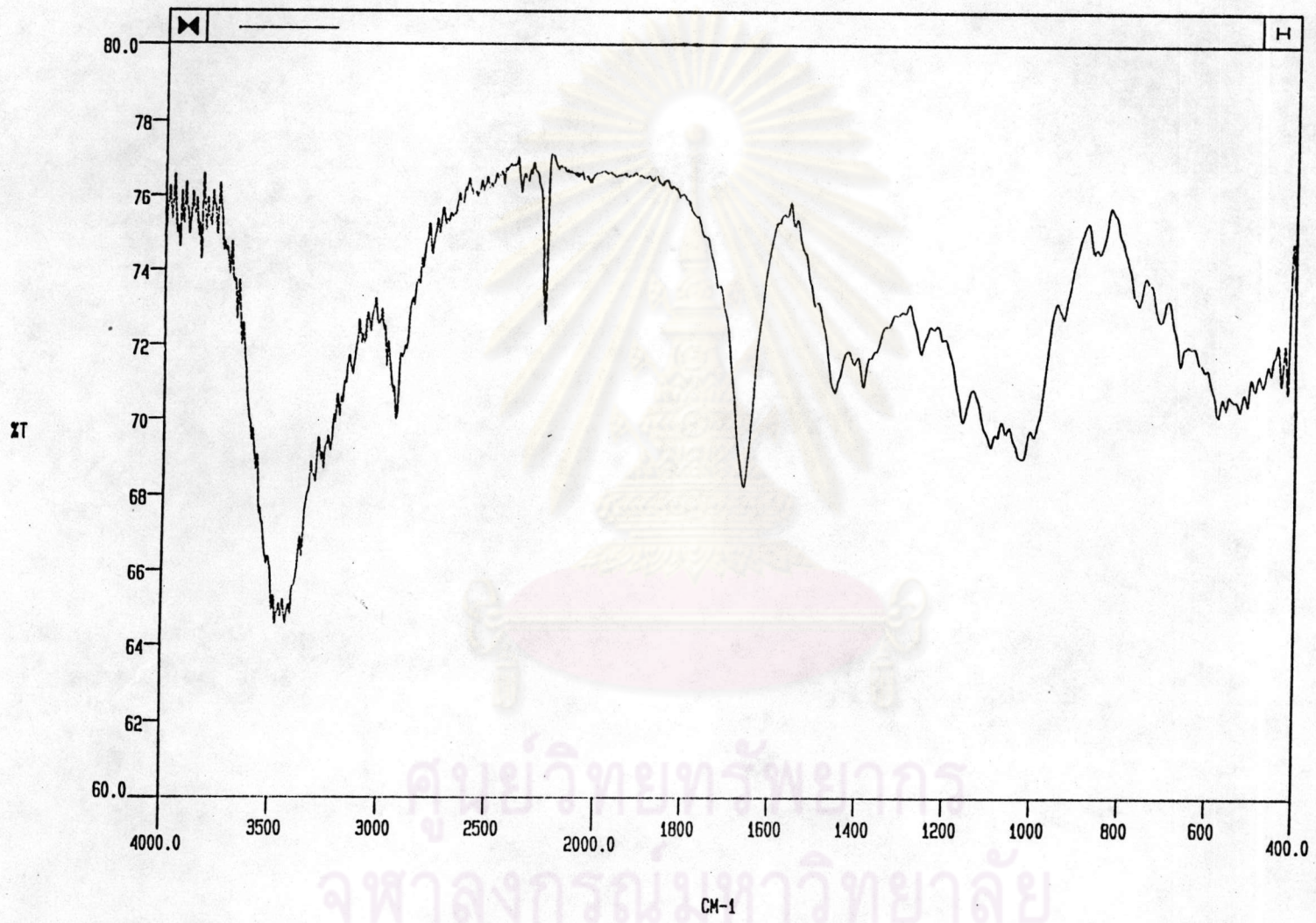Figure 4.2 Infrared spectrum of the graft copolymer after grafting

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Figure 4.3 Infrared spectrum of the graft copolymer after DMF extraction
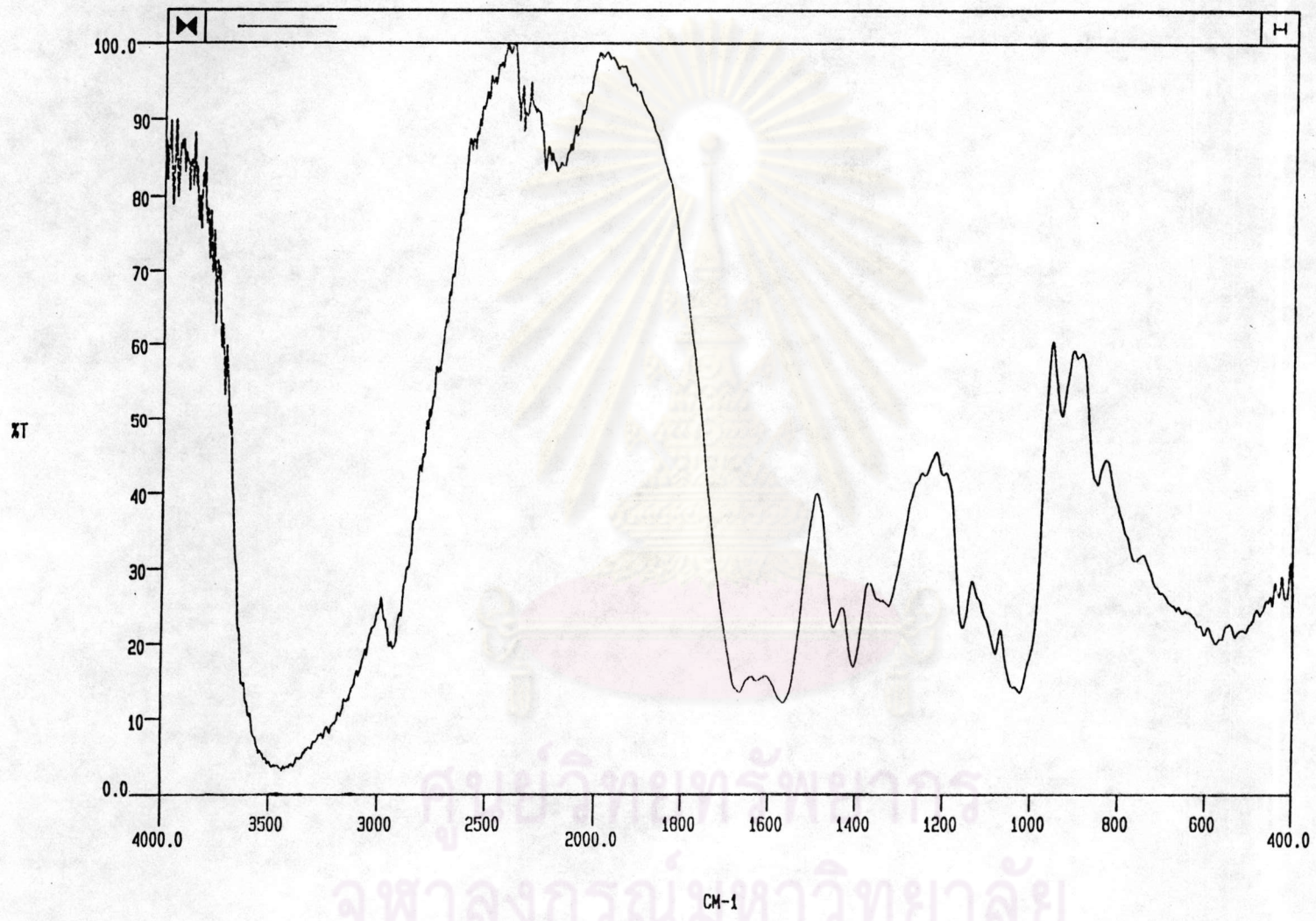
Figure 4.4 Infrared spectrum of the saponified graft copolymer

Table 4.1 The Infrared Absorption of Functional Groups in Cassava Starch, the Copolymers after grafting, after extraction and after saponification.

Starch		Graft copolymer after grafting		Graft copolymer after DMF extraction		HSPAN	
wave number (cm^{-1})	assignment	wave number (cm^{-1})	assignment	wave number (cm^{-1})	assignment	wave number (cm^{-1})	assignment
3,410	O-H stretching	3,410	O-H stretching	3,410	O-H stretching	3,410	O-H stretching
2,931	C-H stretching of CH_2	2,931	C-H stretching of CH_2	2,931	C-H stretching of CH_2	2,931	C-H stretching of CH_2
1,082	C-O stretching	1,082	C-O stretching	1,082	C-O stretching	1,082	C-O stretching
		2,245	$C \equiv N$ stretching (peak area = 0.612)	2,245	$C \equiv N$ stretching (peak area = 0.590)	1,572	C=O stretching of carboxylate
						1,402	C=O stretching of carboxamide

The infrared absorption of cassava starch in Table 4.1 gave the absorption bands at 3,410 and 1,082-1,160 cm^{-1}, the characteristics of amylose containing in the starch. After γ-irradiation of the acrylonitrile onto the starch, one can observe the stretching absorption peak of the C$\equiv$N group containing in acrylonitrile at 2,245 cm^{-1} and the absorption peaks of starch at 3,410 and 1,082-1,160 cm^{-1} still exist. It indicates that acrylonitrile was probably grafted on the starch backbone. Polyacrylonitrile that occurs during the graft copolymerization can be removed by DMF extraction. One can observe the decrease in the peak area of the stretching absorption peak of the C$\equiv$N group at 2,245 cm^{-1}, the appearance of the absorption peak of starch at 3,410 and 1,082-1,160 cm^{-1} shows that starch was the framework of the graft copolymer. Starch-g-PAN was saponified by potassium hydroxide solution to convert the C$\equiv$N the groups of acrylonitrile to the carboxylate and carboxamide groups. The absence of the C$\equiv$N group at 2,245 cm^{-1} and the strong asymmetrical stretching band at 1,572 cm^{-1}, and a weak symmetrical stretching band at 1,402 cm^{-1}, the characteristics of the of the stretching absorption peak of the carboxylate groups and carboxamide groups, respectively was a indicator of the presence of the HSPAN. The absence of the primary amine may be due to a relatively low concentration, and/or the usually low intensity of the NH stretching band and overlapping with the existence of OH stretching of the starting materials. The existence of the absorption peaks of the starch at 3,410 and 1,082-1,160 cm^{-1} still indicates that the saponified PAN was grafted onto the starch backbone.

Grafting of Acrylonitrile onto Cassava Starch

1. Effect of Total Dose on Graft Copolymerization

The result of the gelatinized starch under various total doses exposed by the gamma rays is presented in terms of homopolymer, the grafting

efficiency, the grafting ratio, the conversion of monomer, and percent add-on as shown in Table 4.2.

Table 4.2 Effect of Total Dose (kGy) on the Grafting of Acrylonitrile onto Cassava Starch

Total dose[a] (kGy)	Homopolymer formed (%)	Grafting efficiency (%)	Grafting ratio (%)	Conversion of monomer (%)	Percent add-on (%)
2	12.2	69.6	53.4	47.9	33.0
2.5	11.7	73.1	60.7	51.9	36.2
3	11.0	74.8	65.9	55.0	38.1
3.5	9.7	79.6	75.5	59.3	41.8
4	13.6	71.3	69.3	60.8	39.1
5	20.4	57.5	58.1	63.1	35.8

[a]dose rate 0.25 kGy/min

1.1 Relationship between Total Dose and Percent Homopolymer

Since gamma irradiation usually involves the generation of β-electrons from a cobalt-60 source, and as a consequent, when electrons strike an assembly of organic molecules, many phenomena can be induced. They include:

$$AB \begin{cases} \xrightarrow{\text{dissociation}} A^+, B^-, e^-, A^-, B^+, e^-, \text{etc} \\ \xrightarrow{\bar{e}\ \text{capture}} AB^-, \text{etc} \\ \xrightarrow{\bar{e}\ \text{ejection}} AB^+, 2e^-, \text{etc} \\ \xrightarrow{\text{excitation}} AB^* \longrightarrow A^\bullet + B^\bullet \end{cases} \qquad (4.1)$$
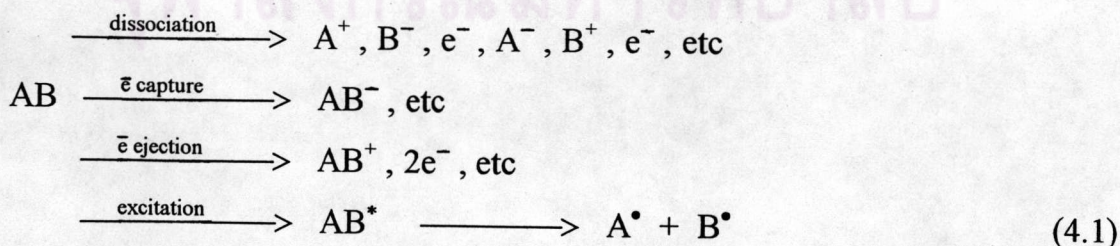
Table 4.2 and Figure 4.5 show the correlation between the total dose and the homopolymer formed. The amount of homopolymer formed varied from 9.6 to 20.4% depending on doses. The lowest homopolymer formed occured at the total irradiation dose of 3.5 kGy; the homopolymer content increased with increasing the amount of total irradiation dose, which was higher than 3.5 kGy. To optimize the formation of graft copolymer with the minimum of the contaminating homopolymer, there are a number of conditions that need to be met. Most importantly, the yield of radicals from radiolysis of polymer (G value) must be, as much as possible, in exess of that from the monomer. Thus the grafting reaction of acrylonitrile onto starch backbone would be favored, since the G(Rad.) from acrylonitrile is about 5-5.6, compared with that of the starch of about 10. This suggests that the higher irradiation dose gave a large amount of radiolysis products (in the absence of oxygen): $H^\bullet$, $OH^\bullet$ and e^-_{aq} of which $G(H^\bullet)$, $G(OH^\bullet)$ and $G(e^-_{aq})$ are 0.55, 2.8 and 2.7 at pH 4-7, respectively, which initiated homopolymerization rather than grafting reaction. The G value or the yield of radicals from radiolysis product, such as solvent of the medium, was closer to the yield of radical from AN than the G value of polymer backbone (5). The H and OH are frequently chain transfer species to growing chains that consequently terminate the grafting reaction. The total irradiation dose at 3.5 kGy is thus just an optimum dose to generate the least amount of $H^\bullet$, $OH^\bullet$ and e^-_{aq} for the chain transfer of homopolymer growing chain.

1.2 Relationship between Total Dose and Grafting Efficiency

Table 4.2 and Figure 4.6 also show that the grafting efficiency is highest at the total irradiation dose of 3.5 kGy. The grafting efficiency decreased with increasing total irradiation dose of those higher than 3.5 kGy, and similarly it decreased with decreasing the total irradiation dose of those lower than 3.5 kGy. It then suggests that the decreasing grafting efficiency is

due to the formation of small fragments of $H^\bullet$, $OH^\bullet$ and e^-_{aq} to form homopolymer at the expense of grafting. A low grafting efficiency, in the other word, a high formation of homopolymer, is not desirable since it would yield a material being composed of a starch backbone grafted with a low amount of the synthetic polymer.

1.3 Relationship between Total Dose and Percent Conversion

Table 4.2 and Figure 4.7 show a continuous increase in percent conversion of the monomer as the amount of total irradiation dose increases. An increase in the total dose enhances the formation of radicals in the reaction mixture: monomer, starch and water. All molecules are activated to induce a higher conversion for both homopolylmer formation and the grafting reaction. Nonetheless, a greater extent of the homopolymer formation occurs at the disposal of graft copolymerization. Appreciable changes in conversion, lower and higher than 59.3%, do not increase the grafting efficiency significantly.

1.4 Relationship between Total Dose and Percent Add-on

The experimental data of the effect of total dose on percent add-on are given in Table 4.2 and in Figure 4.8. The curve indicates that at irradiation doses lower and higher than 3.5 kGy, percent add-on decrease. At the lower end of the irradiation dose, fewer radicals emitted produce a small number of PAN growing chains to be grafted on the fewer active sites of the starch, as there are not enough radicals to initiate ample active sites on the starch backbone. At the higher doses, a greater amount of polyacrylonitrile is formed as homopolymer at the expense of the grafting reaction.
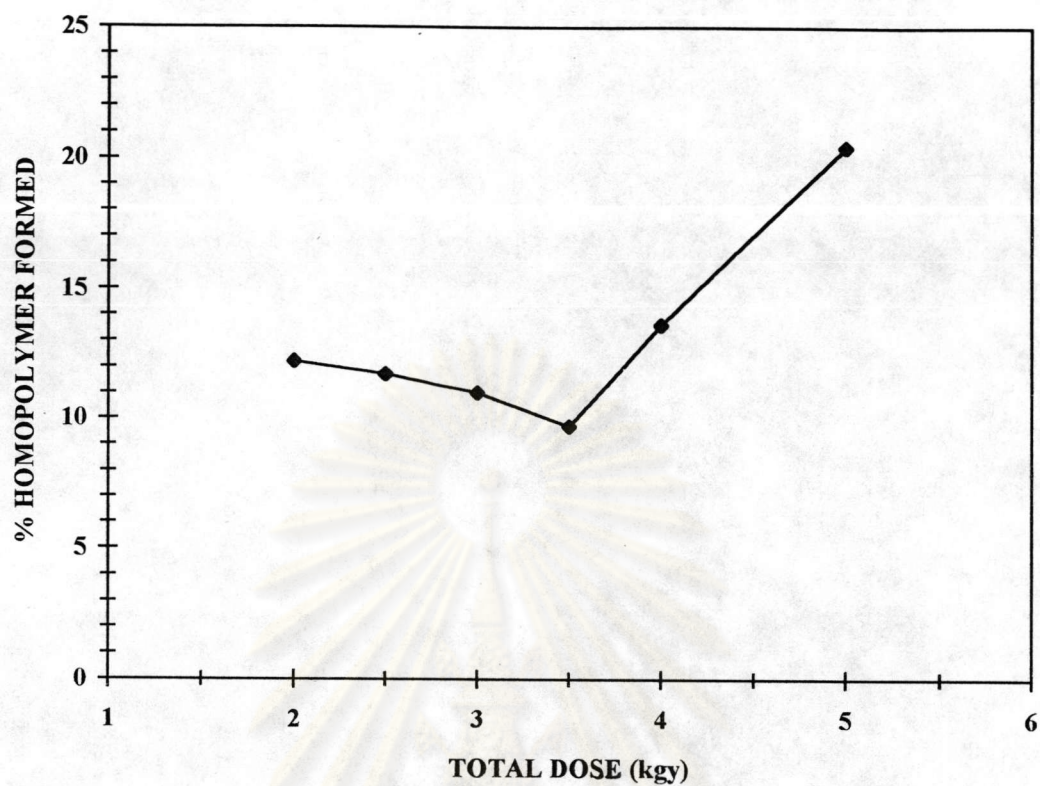
Figure 4.5 Effect of total dose on percent homopolymer
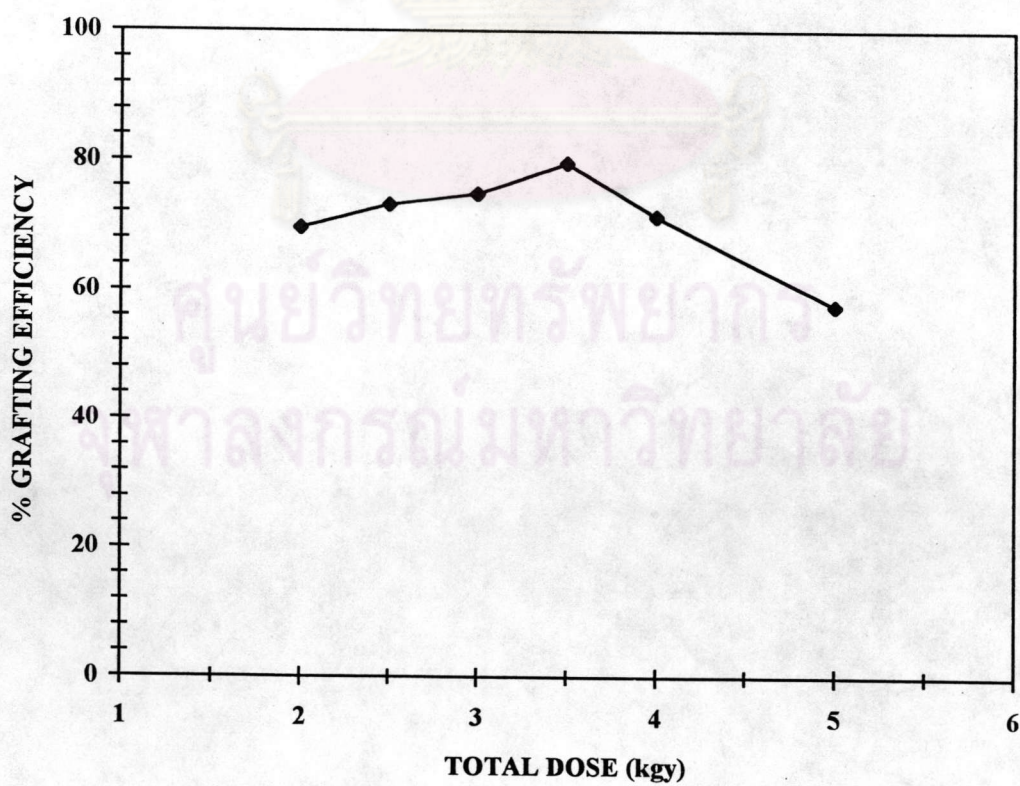

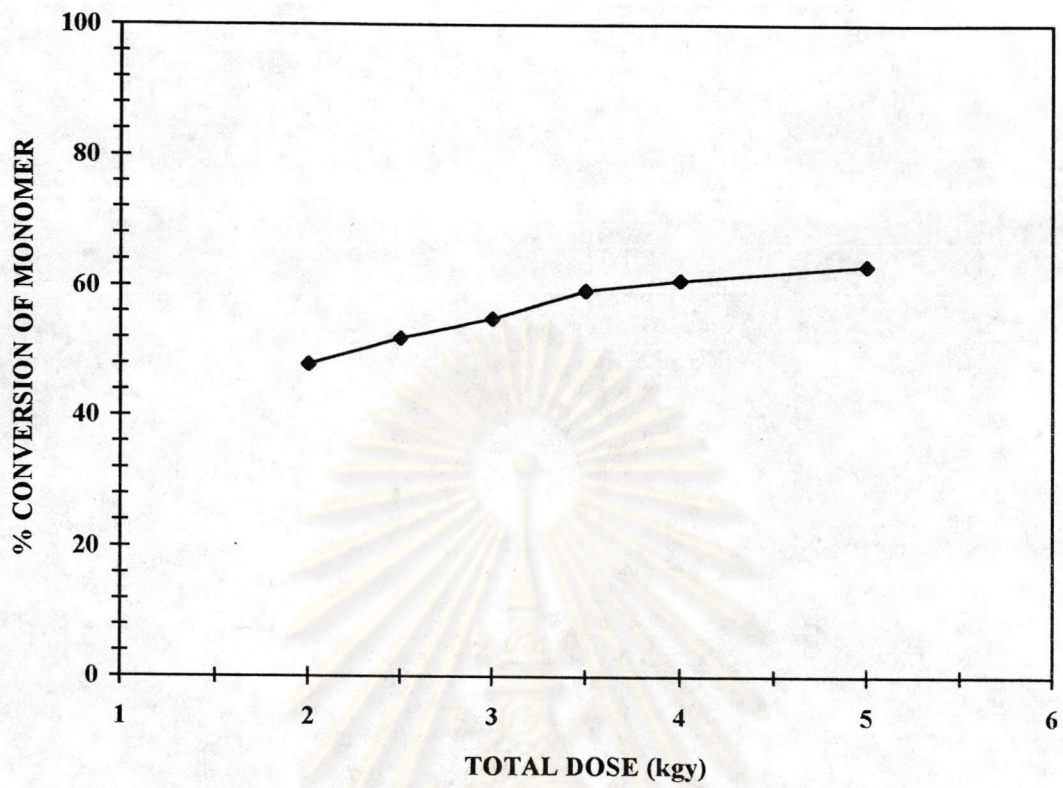Figure 4.6 Effect of total dose on grafting efficiency

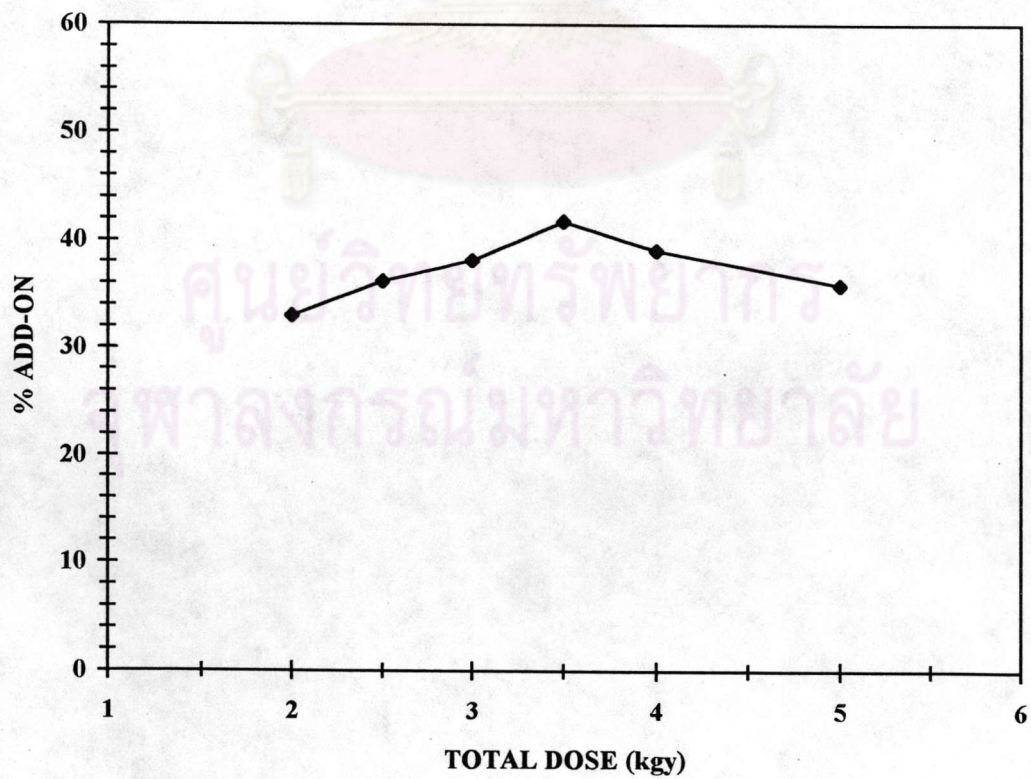Figure 4.7 Effect of total dose on percent conversion

Figure 4.8 Effect of total dose on percent add-on

1.5 Relationship between Total Dose and Grafting Ratio

The grafting ratios of grafted PAN are also shown in Table 4.2 and in Figure 4.9. The results show that the ratio of the number of PAN in grafts to the weight of starch is maximum at the irradiation dose of 3.5 kGy. At lower total doses than 3.5 kGy, there were a small number of PAN growing chains to be grafted on the polymer backbone. Likewise, at higher total doses than 3.5 kGy, radiolysis product induced homopolymerization than grafting reaction.
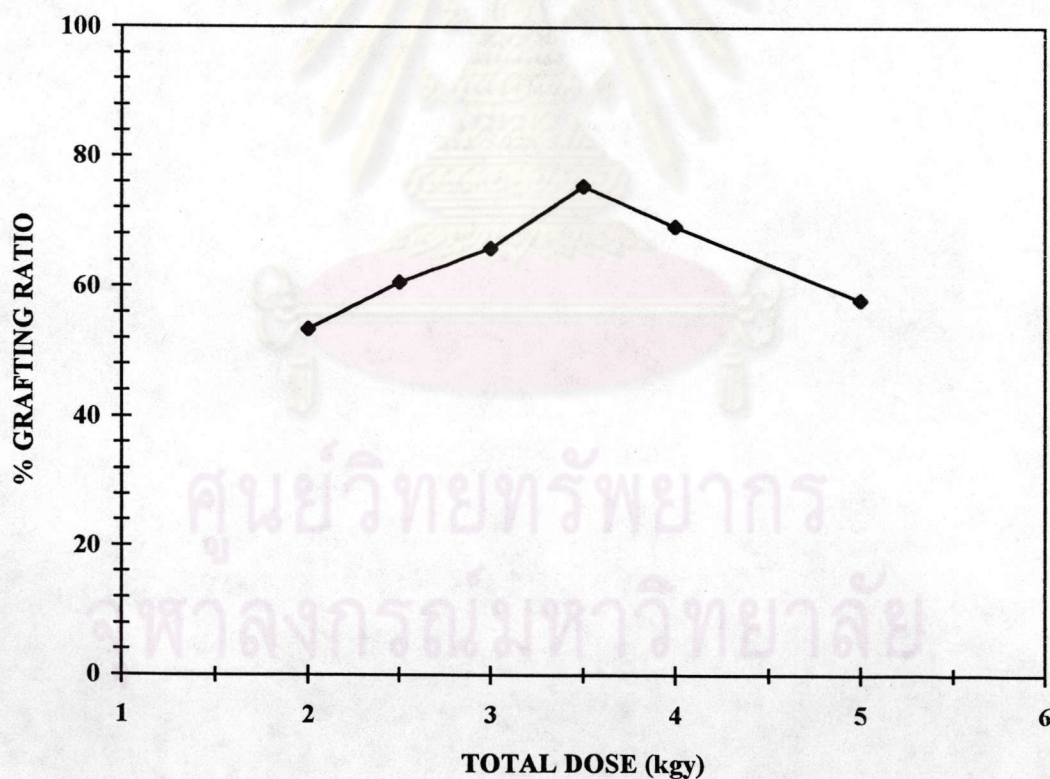

Figure 4.9 Effect of total dose on grafting ratio

1.6 <u>Relationship between Total Dose and Viscosity Average</u>
<u>Molecular Weight and Grafting Frequency</u>

The effect of total irradiation dose on viscosity average molecular weight ($\overline{M}_v$) and grafting frequency (AGU/chain) is given in Table 4.3.

Table 4.3 Effect of Total Dose on Viscosity Average Molecular Weight and Grafting Frequency

Total dose (kGy)	Molecular weight ($\overline{M}_v$)	Grafting frequency (AGU/chain)
2	139,000	1,741
2.5	137,600	1,497
3	134,600	1,346
3.5	132,500	1,139
4	130,700	1,255
5	126,300	1,389

a) Relationship between total dose and viscosity average molecular weight

The average molecular weights of grafted polyacrylonitrile are illustrated in Table 4.3 and Figure 4.10. When increasing the amount of total irradiation dose from 2 to 5 kGy, the $\overline{M}_V$ of grafted PAN decreased gradually from 139,000 to 128,300. The higher the irradiation dose, the more the free radicals are generated to produce a substantial number of short chains of polyacrylonitrile to be grafted on the starch backbones, which result in short grafts with low average molecular weights.

b) Relationship between total dose and grafting frequency

Table 4.3 and Figure 4.11 show the effect of total dose on grafting frequency. The grafting frequency is highest at the total dose of 3.5 kGy. The higher the grafting frequency, the lower the number of AGU/chain. At lower total dose than 3.5 kGy, there were not enough PAN growing chains to be grafted on the polylmer backbone. Likewise, at higher total dose than 3.5 kGy, too many PAN radicals induced by radiolysis were produced and such radicals favored homopolymer formation due to diffusion predominance and thus less grafting reaction onto starch backbones.

1.7 Relationship between Water Absorption and Total Dose

Water absorption in deionized distilled water by the saponified starch-g-polyacrylonitrile is shown in Table 4.4 and Figure 4.12.

Table 4.4 Deionized Distilled Water Absorption as a Function of Total Dose

Total dose (kGy)	Water absorption in deionized distilled water (g/g)
2	289
2.5	353
3	420
3.5	500
4	459
5	396

The experimental data in Table 4.4 show that at the total dose of 3.5 kGy, the highest water absorption is obtained.
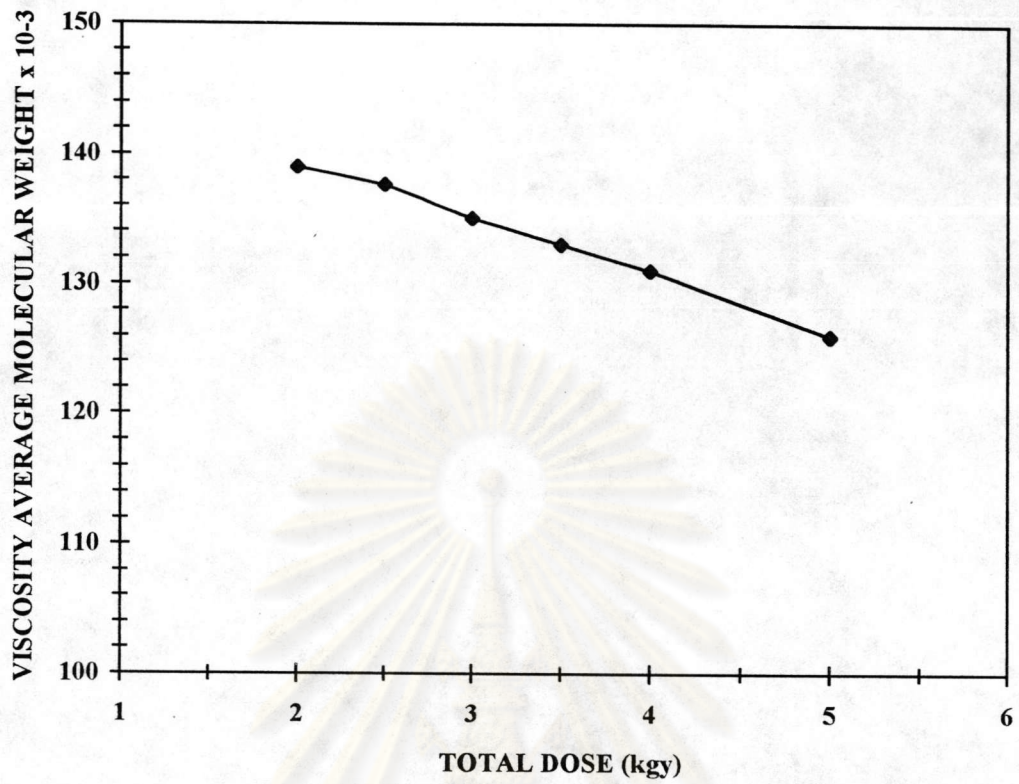
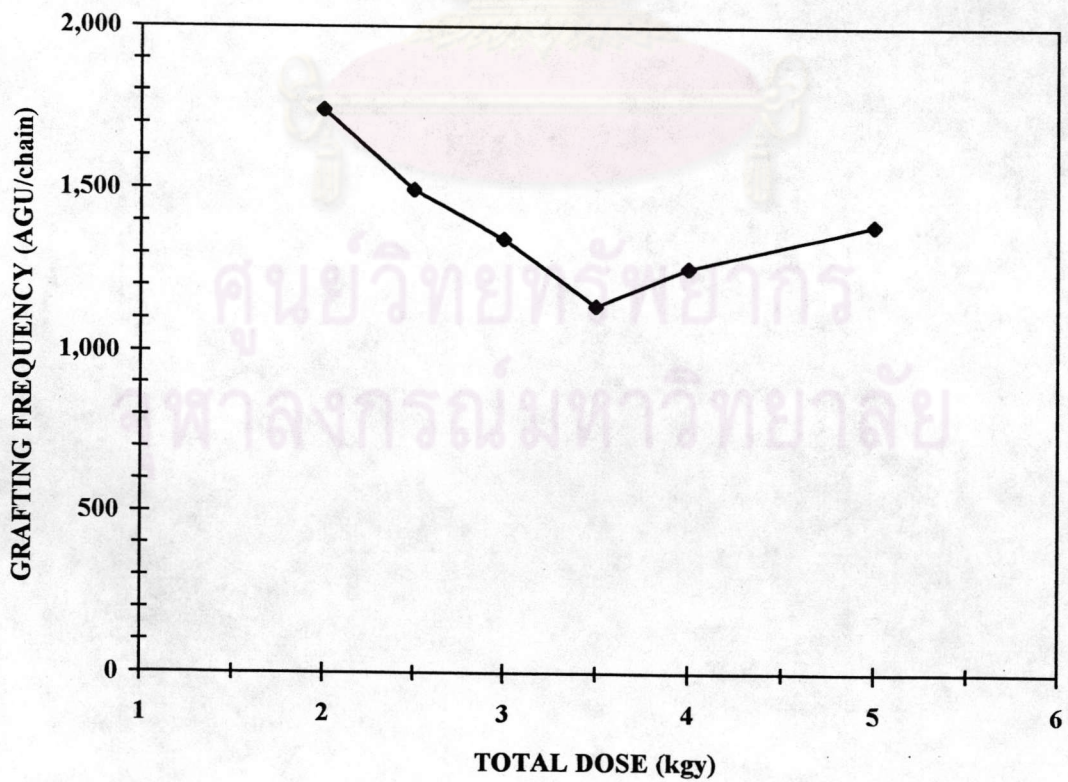Figure 4.10 Effect of total dose on viscosity average molecular weight

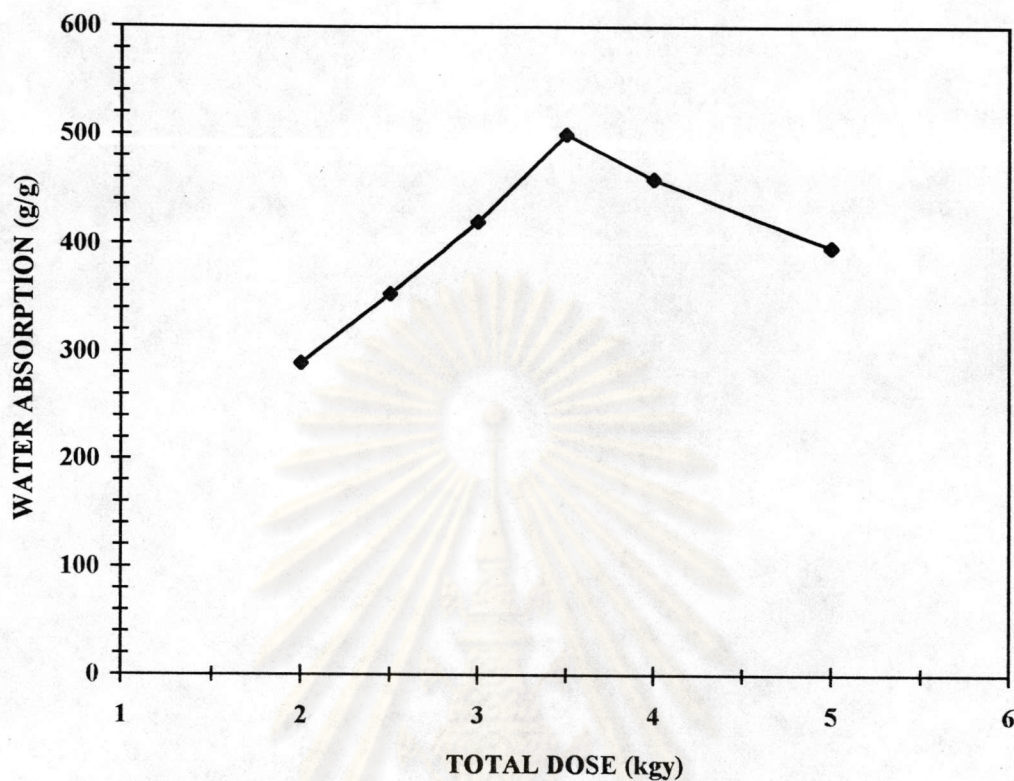Figure 4.11 Effect of total dose on grafting frequency

Figure 4.12 Effect of total dose on water absorption

2. Effect of Metal Sheet on Reduction of Homopolymer

From the previous research (22), the aluminium foil was found to suppress homopolymerization. This research studied the effect of the different kinds of metal sheets such as aluminium foil, copper sheet, lead sheet and zinc sheet in reducing homopolymer. The result of metal sheets on graft copolymerization is presented in Table 4.5.

Table 4.5 Effect of Metal Sheets on the Grafting of Acrylonitrile onto
Cassava Starch

Metal Sheet[a]	Homopolymer formed (%)	Grafting efficiency (%)	Grafting ratio (%)	Conversion of monomer (%)	Percent add-on (%)
Al	9.68	79.5	75.5	59.3	41.8
Cu	10.15	78.3	73.4	58.6	40.9
Pb	10.43	77.7	72.6	58.4	40.5
Zn	11.58	74.8	65.2	54.5	38.8

[a]total dose 3.5 kGy

2.1 Relationship between Grafting Parameters and Metal Sheet

Metal sheet has the capability of reducing homopolymer formed during graft copolymerization. Since the absorption of gamma rays of metal sheet leads to electron emission, the increased electrons bring about more primary product. The increase in $H^•$ and $^•OH$ radicals can increase grafting sites of the starch backbone by hydrogen abstraction.

Table 4.5 indicates the efficient effect of aluminium foil in reducing homopolymer. It may be due to the purity of metal sheets. In fact, copper plate and lead sheet systems give a little higher homopolymer formed than does aluminium foil. The inclusion of the zinc plate gives the highest homopolymer formed because the zinc plate used is the construction grade. Impurities in the zinc plate may be anticipated to interfere the result.

Besides giving the least homopolymer formed, aluminium foil provides the most grafting efficiency, grafting ratio and percent add-on.

Table 4.6 Physical Properties of Aluminium, Copper, Lead and Zinc

	Aluminium	Copper	Lead	Zinc
Electronic configuration	$[Ne]3s^2$ $3p^1$	$[Ar]3d^{10}$ $4s^1$	$[Xe]4f^{14}$ $5d^{10} 6s^2 6p^2$	$[Ar]3d^{10} 4s^2$
Oxidation state	$1, 3^*$	$1, 2^*$	$2^*, 4$	2
Ionization potential, eV				
I	5.98	7.68	7.42	9.39
II	18.82	20.34	15.03	17.96
III	28.44	29.50	31.93	39.70

* the most stable oxidation state

From the electronic configuration value, aluminium has the core of Ne with two electrons at the s-orbital and one p-electron at the outermost orbital (valence electrons) so that the maximum valence displayed by aluminium is three. The valence of zinc is invariably two. That of copper is one and it can release one electron in d-orbital so the stable oxidation state is two. Since lead has four electrons in its valence shell, the element would be expected to show a normal valence of four. However, the two s-electrons of lead are reluctant to ionize and are thus sometimes referred to as the inert pair. When gamma rays interact with metal sheets, they lead to electron emission of metal sheets depending on the extent of total dose and ionization potential. The aluminium foil can easily generate β-electron upon irradiation. Suppression of homopolymer takes place through the radical termination possibly by a redox reaction between the H• and •OH and the aluminium atom, or an electron transfer from the polymer growing chains to a p-orbital of the aluminium ion. Electrons ejected in the ionization process participate in the primary species in

solution. This may bring about the promotion in the H-abstraction of starch molecule so the grafting reaction is enhanced.

2.2 Relationship between Viscosity Average Molecular Weight and Grafting Frequency and Metal Sheet

The effect of the different kinds of metal sheets on the viscosity average molecular weight and grafting frequency is shown in Table 4.7.

Table 4.7 Effect of Metal Sheets on Viscosity Average Molecular Weight and Grafting Frequency

Metal sheet	Molecular weight (M_v)	Grafting frequency (AGU/chain)
Al	132,500	1,139
Cu	129,000	1,153
Pb	130,200	1,179
Zn	128,400	1,249

From the above table, the average molecular weight varies from 132,500 to 128,400 and grafting frequency differs from 1,139 to 1,249. The alumiunium foil can produce the product with the highest percent add-on, while the average molecular weight of the grafted PAN is also the highest.

2.3 Relationship between Water Absorption and Metal Sheet

The effect of the metal sheet on water absorption in deionized distilled water by saponified starch-g-PAN is shown in Table 4.8 and Figure 4.13.

Table 4.8 Effect of Metal Sheets on Deionized Distilled Water Absorption

Metal sheet	Water absorption in deionized distillated water (g/g)
Al	500
Cu	480
Pb	467
Zn	367

The results show that the highest water absorption can be achieved by using the aluminium foil to cover the inner wall of the irradiated vessel.
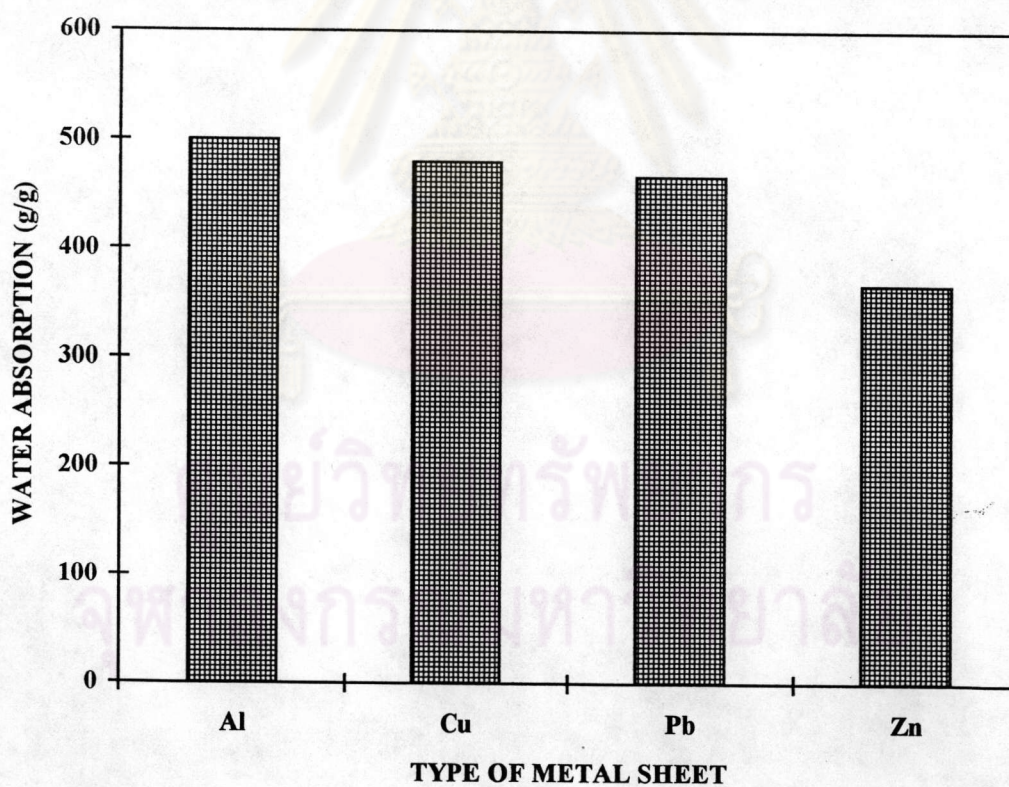

Figure 4.13 Effect of the metal sheets on deionized distilled water absorption

3. Effect of the Methyl Ether Hydroquinone (MEHQ) Inhibitor on Graft Copolymerization

According to the results of total dose and metal sheets appropriate for graft copolymerization of AN onto cassava starch, the total dose of 3.5 kGy with the coverage of the aluminium foil on the inner wall of the irradiated tube was found to provide the maximum water absorption in deionized distilled water.

The effects of the MEHQ inhibitor, on the homopolymer formed, percent add-on, the conversion of the monomer, the grafting efficiency, and the grafting ratio are tabulated in Table 4.9.

Table 4.9 Effect of the MEHQ Inhibitor on Graft Copolymerization of Acrylonitrile onto Cassava Starch

Inhibitor[a] (%wt based on monomer)	Homopolymer formed (%)	Grafting efficiency (%)	Grafting ratio (%)	Conversion of monomer (%)	Percent add-on (%)
0 (control)	9.7	79.6	75.5	59.3	41.8
0.00125	12.9	72.5	65.4	56.4	38.9
0.0025	14.3	68.5	59.1	53.9	36.2
0.005	18.0	59.0	48.0	50.9	31.6
0.01	24.6	42.7	33.0	48.3	24.3
0.02	28.9	32.0	23.9	46.7	19.1

[a]total dose 3.5 kGy, aluminium foil was used for covering the inner wall of the irradiated vessel.
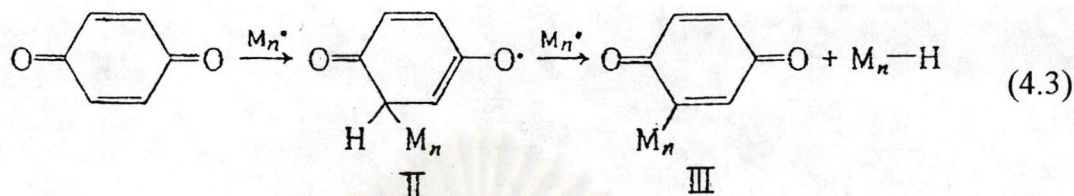
3.1 Relationship between the MEHQ Inhibitor and Percent

Homopolymer

Table 4.9 and Figure 4.14 show the effect of the MEHQ inhibitor on the extent of homopolymer formation. The result shows that the percentage of homopolymer formed increases as the concentration of inhibitor increases. Inhibitor stops every radical by reacting with the initiating and propagating radicals and converting them either to nonradical species or radicals with low reactivity to undergo propagation(30). In this case, the inhibitor can dissolve in both monomer phase and aqueous phases but it can disperse in aqueous phase more than monomer phase because of the strong H-bonding between it and water(31-33). Thus, when the inhibitor in monomer phase mixed thoroughly with aqueous phase, the inhibitor can partition into the aqueous phase, which increases the efficiency in suppressing the radicals in aqueous phase and starch. Nonetheless, the neat monomer and the residue inhibitor containing monomer can produce homopolymer but at a different extent. The mechanism for suppressing the radicals may be proposed that methyl ether hydroquinone can rearrange their form to quinone upon γ-irradiation. The behavior of quinone is quite complex. Two major types of reaction product are obtained as quinone and ether, formed by reaction at the C and O atoms of the quinone, respectively. Attacks of the starch and propagating radicals at the oxygen atom yield the aryloxy radical, I, which can terminate by coupling and/or disproportionation with another propagating radical (or itself) or add the monomer. Attack on the ring carbon yields

$$M_n^{\bullet} + O{=}\langle\rangle{=}O \rightarrow M_n{-}O{-}\langle\rangle{-}O^{\bullet}$$

(4.2)

I
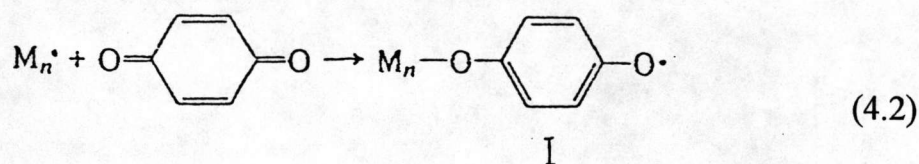
radical, II, which can react with other starch and propagating radicals (Eq. 4.3) to form the quinone with the polymer side chain, III. The latter itself may be an

inhibitor as well. An alternate route for radical II is rearrangement to IV followed by coupling or termination with other radicals (30).

$$(4.3)$$

$$(4.4)$$

3.2 Relationship between the MEHQ Inhibitor and Percent Grafting Efficiency

The experimental data showing the effect of the MEHQ inhibitor on grafting efficiency are given in Table 4.9 and Figure 4.15. The data show that the lowest grafting efficiency is obtained with the highest concentration of the inhibitor. Since the inhibitor that is fond of living in aqueous phase and reacts with starch and propagating radicals suppresses grafting reaction, grafting sites reduced and grafted chains was short. Monomer was grafted less and then could homopolymerize readily. Thus, grafting efficiency decreases.

3.3 Relationship between the MEHQ Inhibitor and Percent Conversion of the Monomer

The correlation between the conversion of monomer on the amount of the inhibitor is shown in Table 4.9 and Figure 4.16. It indicated the conversion of the monomer was decreased as the amount of inhibitor increased because of the enhancement of the suppression of polymerizations.
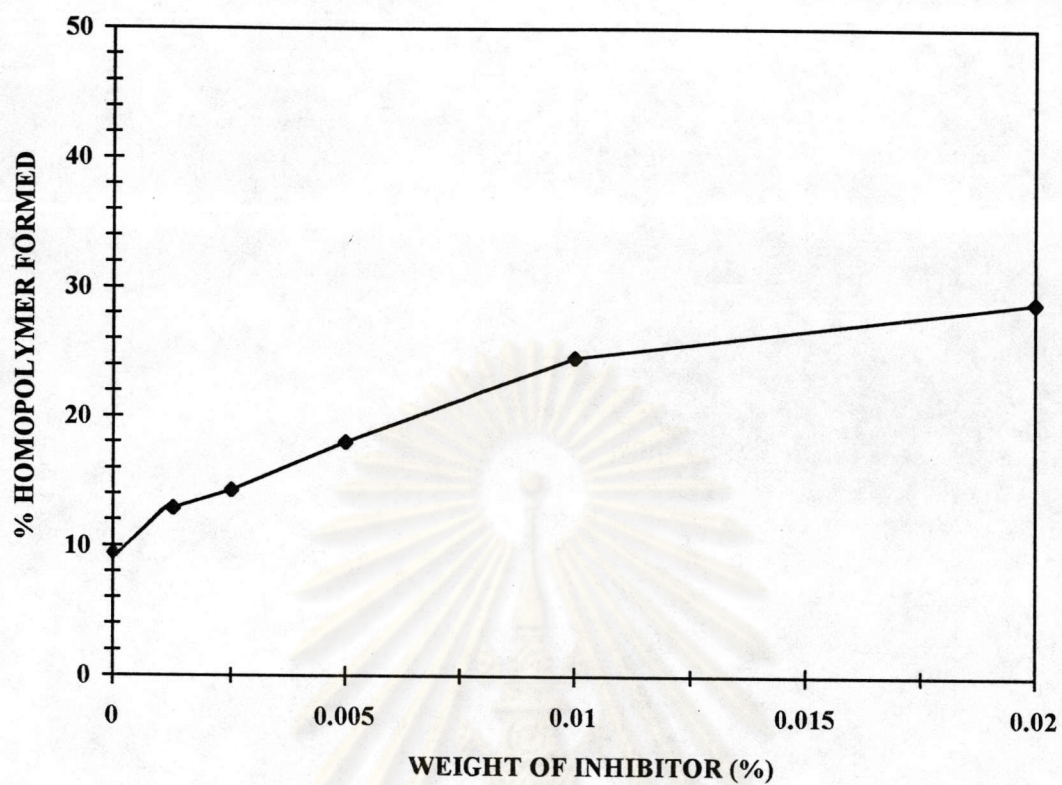
71

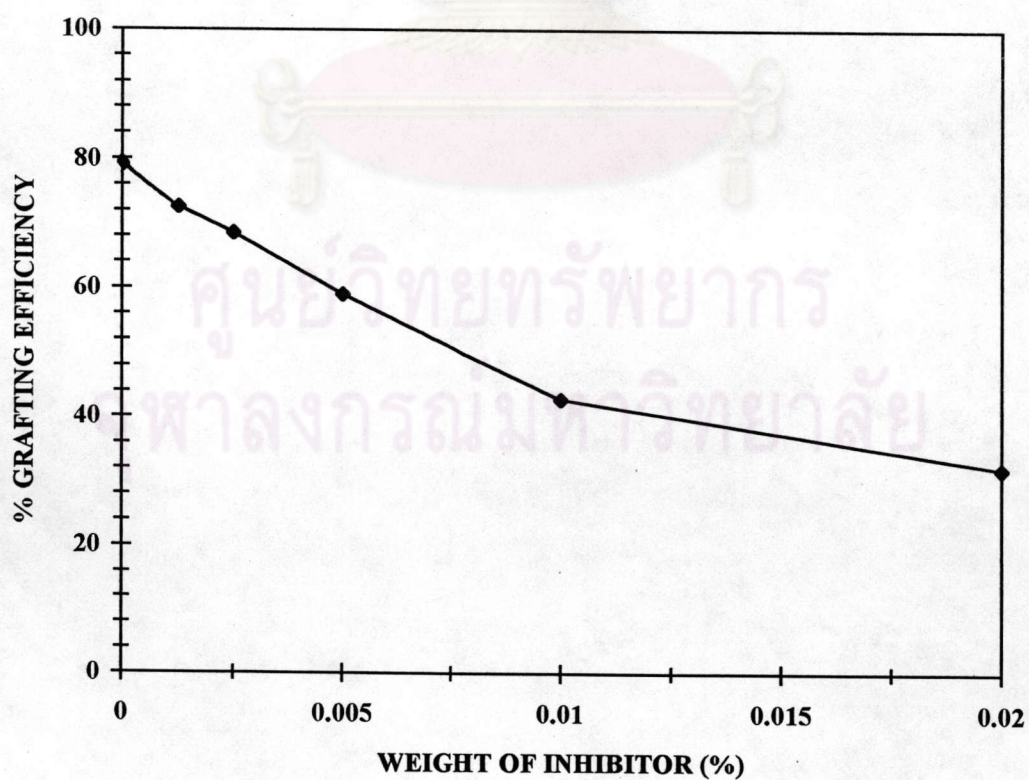Figure 4.14 Effect of the MEHQ inhibitor on percent homopolymer

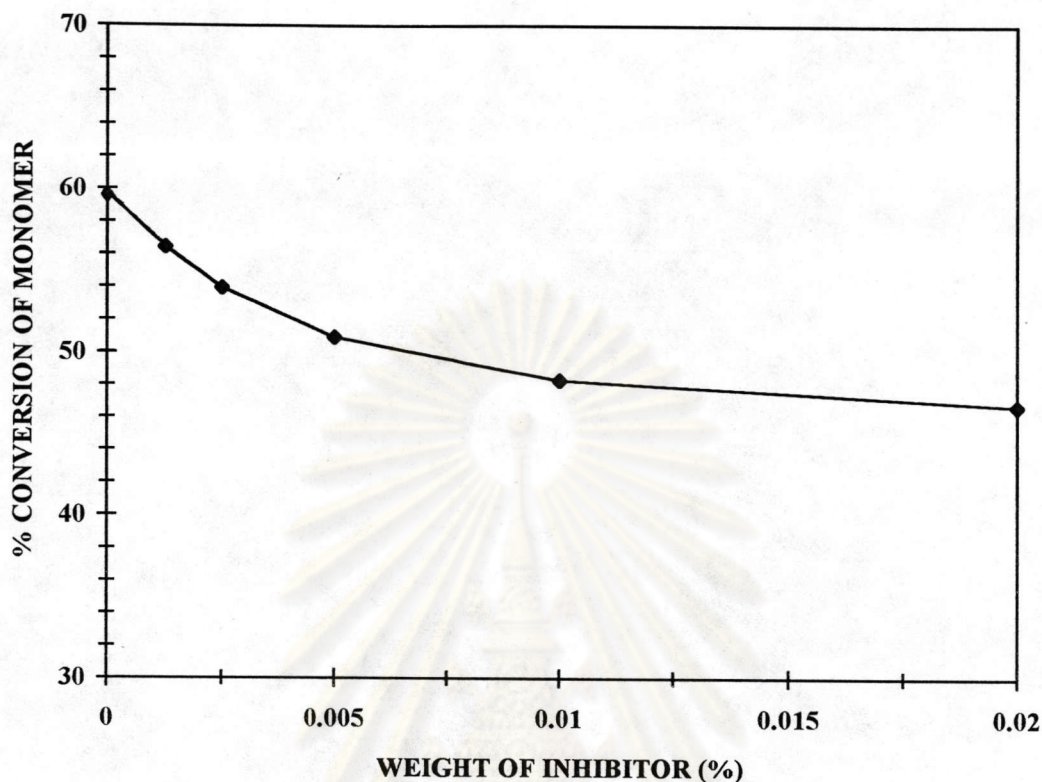Figure 4.15 Effect of the MEHQ inhibitor on percent grafting efficiency

Figure 4.16 Effect of the MEHQ inhibitor on percent conversion of

monomer

3.4 <u>Relationship between the MEHQ Inhibitor and Percent Add-on</u>

The effect of the MEHQ inhibitor on percent add-on is given in Table 4.9 and Figure 4.17. The results show that there is a continuous decrease in % add-on as the amount of the inhibitor increases.

3.5 <u>Relationship between the MEHQ Inhibitor and Grafting Ratio</u>

Figure 4.18 and Table 4.9 show the effect of the MEHQ inhibitor on grafting ratio. Grafting Ratio is the ratio between the weight of grafted PAN and starch. It indicates that grafting ratio decreases when the amount of the inhibitor increases. As the amount of the inhibitor in aqueous phase increases, the grafted PAN decreases that results in a reduction in percent grafting ratio.
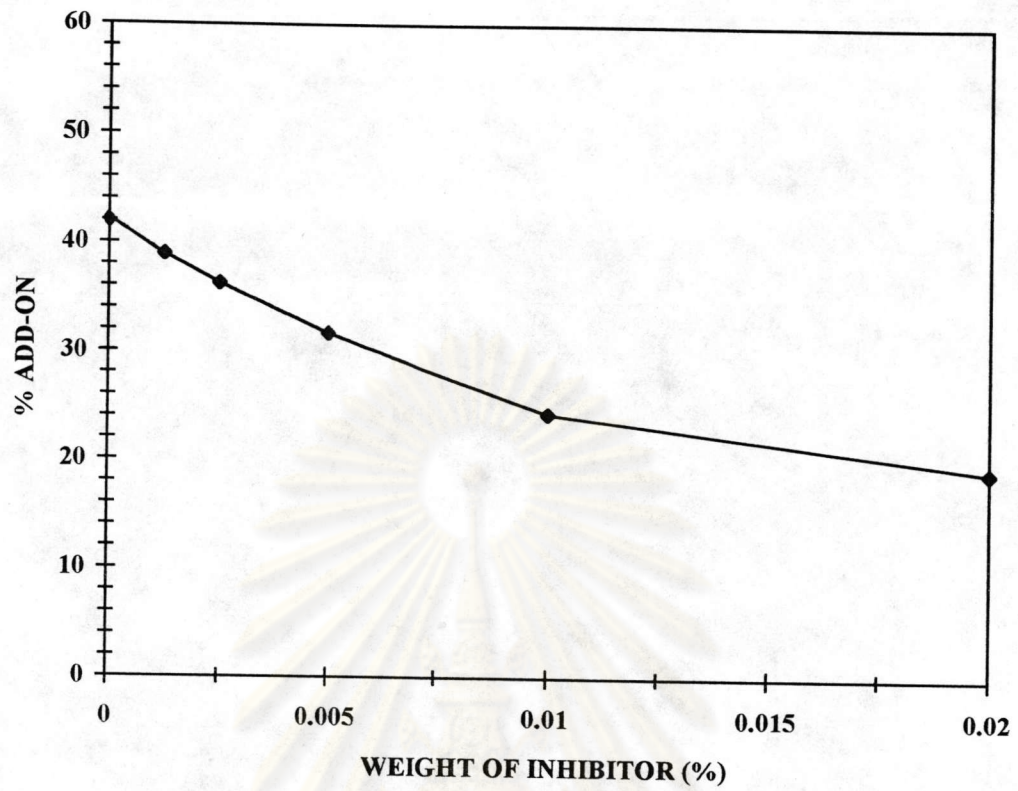
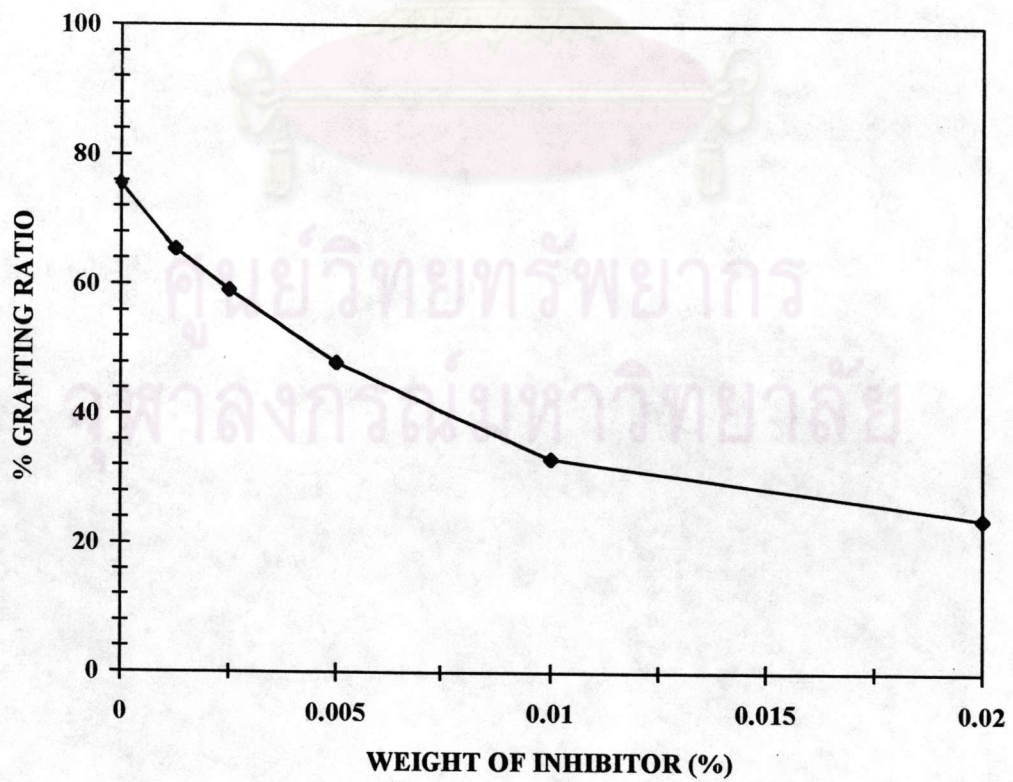Figure 4.17 Effect of the MEHQ inhibitor on percent add-on

Figure 4.18 Effect of the MEHQ inhibitor on grafting ratio

3.6 <u>Relationship between Viscosity Average Molecular Weight,</u>
<u>Grafting Frequency and the MEHQ Inhibitor</u>

The data of the effect of the amount of the MEHQ inhibitor on the viscosity average molecular weight ($\overline{M}_v$) and the grafting frequency are given in Table 4.10.

Table 4.10 Effect of the MEHQ Inhibitor on Viscosity Average Molecular Weight ($\overline{M}_v$) and Grafting Frequency

Inhibitor (%wt based on the monomer)	Molecular weight ($\overline{M}_v$)	Grafting frequency (AGU/chain)
0 (control)	132,500	1,139
0.00125	117,900	1,143
0.0025	106,300	1,160
0.005	95,500	1,278
0.01	78,300	1,508
0.02	64,000	1,677

a) Relationship between the MEHQ Inhibitor and Viscosity Average Molecular Weight

Figure 4.19 and Table 4.10 illustrate the effect of the amount of the MEHQ inhibitor on the viscosity average molecular weight ($\overline{M}_v$) of grafted PAN. Since the addition of the inhibitor suppresses the graft-polymerization of monomers, the viscosity average molecular weight of grafted PAN decreases.

b) Relationship between the MEHQ Inhibitor and Grafting Frequency

Figure 4.20 shows the effect of the MEHQ inhibitor on grafting frequency. The result shows that the grafting frequency decreased while the concentration of the inhibitor increased. It may be attributed to that the inhibitor is participated in the aqueous phase that has an effect on the number of active sites on the starch backbone.

3.7 Relationship between the MEHQ Inhibitor and Water Absorption

The effect of the MEHQ inhibitor on water absorption in deionized distilled water by the saponified starch-g-PAN is shown in Table 4.11 and Figure 4.21.

Table 4.11 Effect of the MEHQ Inhibitor on Water Absorption in Deionized Distilled Water

Inhibitor (%wt based on the monomer)	Water absorption in deionized distilled water (g/g)
0 (control)	500
0.00125	431
0.0025	324
0.005	280
0.01	232
0.02	172

The results show that the water absorption was of 431 times it dried weight obtained at the amount of the inhibitor of 1.25×10^{-3} % weight. It indicates that the increase in the amount of the inhibitor decreasing the grafted PAN chains results in the decrease in the water absorption.
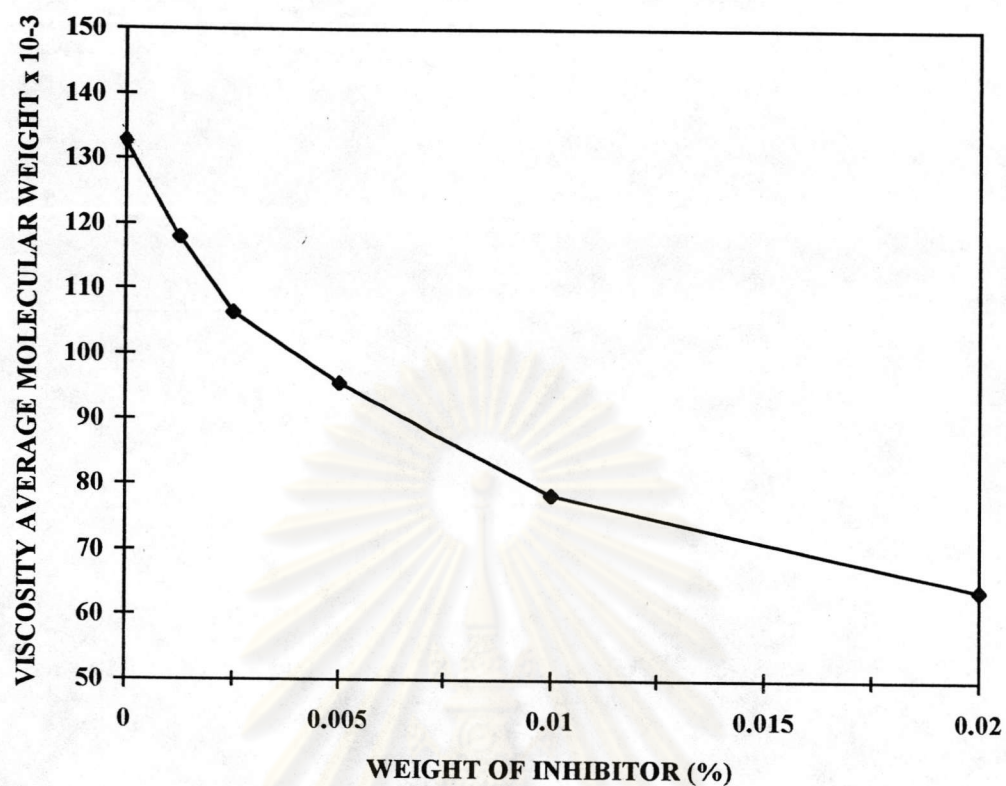
Figure 4.19 Effect of the MEHQ inhibitor on viscosity average molecular weight
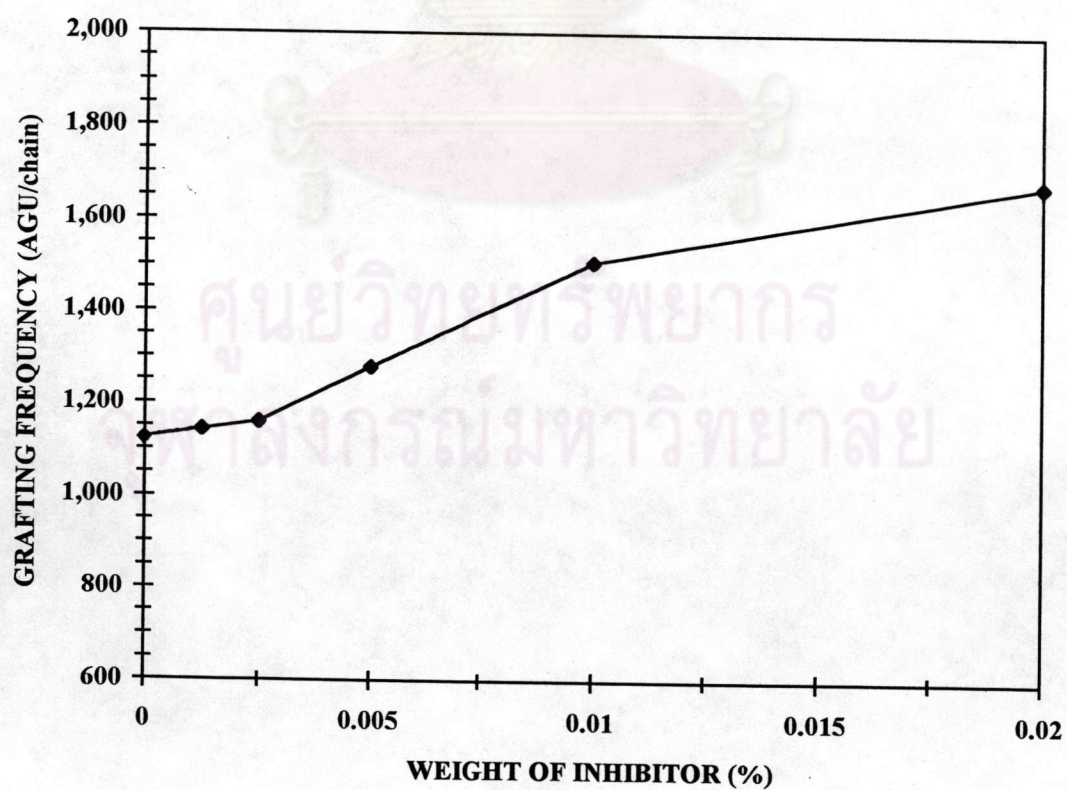

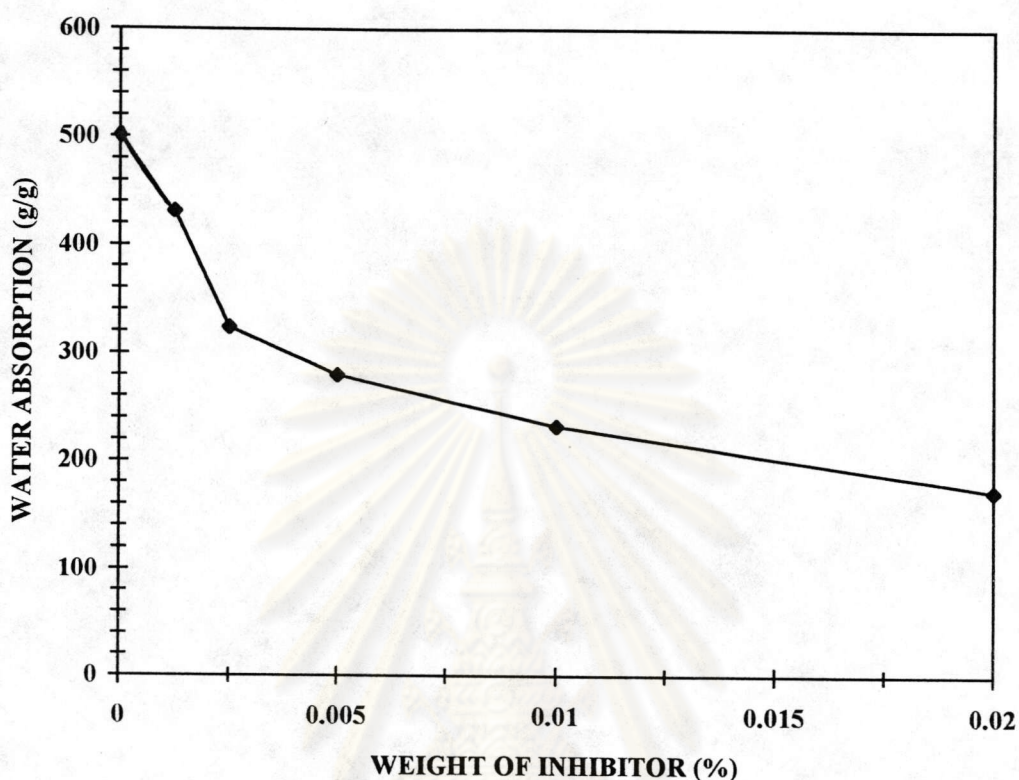Figure 4.20 Effect of the MEHQ inhibitor on grafting frequency

Figure 4.21 Effect of the MEHQ inhibitor on water absorption

in deionized distilled water

4. <u>Effect of Nitric Acid on Graft Copolymerization</u>

Grafting parameters of acrylonitrile grafted onto cassava starch with and without acid solution (0.1 M HNO_3) are shown in Table 4.12.

In acid media, the radiolysis of water leads to an increase in $G(H^\bullet)$. This process can then lead to increased grafting sites on the starch backbone by hydrogen abstraction reactions (26). It causes more acrylonitrile graft on the starch, thus grafting efficiency, grafting ratio, percent add-on all are increased and the homopolymer decreases accordingly.

Table 4.12 Effect of Acid on Grafting of Acrylonitrile onto Cassava Starch

	Homopolymer formed (%)	Grafting efficiency (%)	Grafting ratio (%)	Conversion of monomer (%)	Percent add-on (%)
with acid	5.6	88.1	81.7	58.0	43.3
without acid	9.7	79.6	75.5	59.3	41.8

[a]total dose 3.5 kGy, aluminium foil for covering the inner wall of the irradiated vessel

Conversion of monomer is rather constant. At the total dose given, the ionizing radiation can initiate a certain number of free radicals that are used both for homopolymerization and graft copolymerization in a proper ratio.

Table 4.13 Effect of Acid on Viscosity Average Molecular Weight ($\overline{M}_v$) and Grafting Frequency

	Molecular weight ($\overline{M}_v$)	Grafting frequency (AGUs/chain)
with acid	129,400	1,047
without acid	132,500	1,139

The molecular weight data are summarized in Table 4.13. The data show that viscosity average molecular weight of the grafted polyacrylonitrile decreases when the acid is added in the irradiated solution. Acid plays an important role in enhancing grafting sites on the starch backbones. The grafting frequency, therefore, increases according to the large number of grafting sites. The molecular weight of the grafted PAN is less dependence on the presence of the acid, the grafted chains seem to be shorter in the presence of

the acid that is caused at the expense of the higher frequency in grafting (1,047 AGUs/chain).

Table 4.14 Effect of the acid on Water Absorption in Deionized Distilled Water

	Water absorption in deionized distillated water (g/g)
with acid	550
without acid	500

The effect of the acid solution, added to the gelatinized starch before mixing with AN, on water absorption in deionized distilled water by the saponified starch-g-PAN compared with neutral solution is exhibited in Table 4.14.

5. Effect of Comonomer on Graft Copolymerization

The effect of styrene as a comonomer for graft copolymerization of acrylonitrile on the starch is indicated in Table 4.15.

Table 4.15 Effect of Styrene on Graft Copolymerization of Acrylonitrile onto Cassava Starch

Total dose[a] (kGy)	Homopolymer of acrylonitrile (%)	Homopolymer of styrene (%)	Water absorption (g/g)
3.5	11.2	2.8	443
7	18.0	4.1	369
10	24.6	6.5	319

[a]AN = 20 ml, S = 5 ml

The experimental data indicated that the homopolymer of styrene formed is smaller because the G value of styrene ($G_s = 0.69$) is so low compared to that of acrylonitrile ($G_{AN} = 5\text{-}5.6$) (4), that styrene cannot self-polymerize at low dose. On the other hand, the reactivity ratio of styrene radical is higher than that of acrylonitrile ($r_S = 0.4$, $r_{AN} = 0.04$) (30), styrene can graft copolymerize with the starch before acrylonitrile. Thus, the grafted chains have both styrene and acrylonitrile molecules that decrease the water absorption. It may be due to that the grafted chains have low carboxylate groups, which is derived from the hydrolysis of acrylonitrile with potassium hydroxide solution. The grafted chains of both polystyrene and polyacrylonitrile have become stiffer imposed by the bulky phenyl group of styrene. In addition, two grafted polystyrene chains may undergo intra- or intermolecular crosslinking that introduce a very rigid network, which is difficult to swell in fluids. If a higher dose were applied, both styrene and acrylonitrile could have promoted more homopolymerization but the latter could have homopolymerized more than the former because of its higher G-value and the higher concentration of acrylonitrile in solution.

6. Effect of The Quantity of AN (ml) on Graft Copolymerization

According to the results of the total dose of 3.5 kGy, the graft copolymer prepared by aluminium foil for covering the inner wall of the irradiated tube and nitric acid for enhancement of graft copolymerization of AN onto cassava starch were found to provide the maximum water absorption in deionized distilled water.

Table 4.16 gives the data of percent add-on, the grafting efficiency, the grafting ratio, the homopolymer formed, and the conversion of the monomer obtained at the various quantities of AN(ml).

Table 4.16 Effect of The Quantity of AN(ml) on Graft Copolymerization
of Acrylonitrile onto Cassava Starch.

AN^a (ml)	Homopolymer formed (%)	Grafting efficiency (%)	Grafting ratio (%)	Conversion of monomer (%)	Percent add-on (%)
10	2.5	92.0	43.4	58.9	28.7
15	4.1	90.1	63.2	58.5	37.6
20	5.6	88.1	81.7	58.1	43.3
25	9.5	81.9	94.3	57.6	47.4

^{a}total dose 3.5 kGy, aluminium foil for covering inner wall of the irradiated tube, in the presence of nitric acid

6.1 Relationship between The Quantity of AN(ml) and Percent Homopolymer

The percentage of homopolymer formed varied from 2.5 to 9.5% as the quantity of acrylonitrile increased from 10 to 25 ml. The corresponding percentage of homopolymer was depicted in Figure 4.22. The effect of high monomer quantity leads to the more homopolymerization. More AN molecules could be activated easily in the monomer phase to yield $AN^•$ that might terminate through collision due to crowdiness.

6.2 Relationship between The Quantity of AN(ml) and Grafting Efficiency

The effect of the quantity of AN(ml) ratio on grafting efficiency is given in Table 4.16 and illustrated in Figure 4.23. The result shows that the highest grafting efficiency was obtained with the lowest quantity of acrylonitrile. It decreased from 92.0 to 81.9% as the quantity of acrylonitrile was increased from 10 to 25 ml. The effect of high monomer
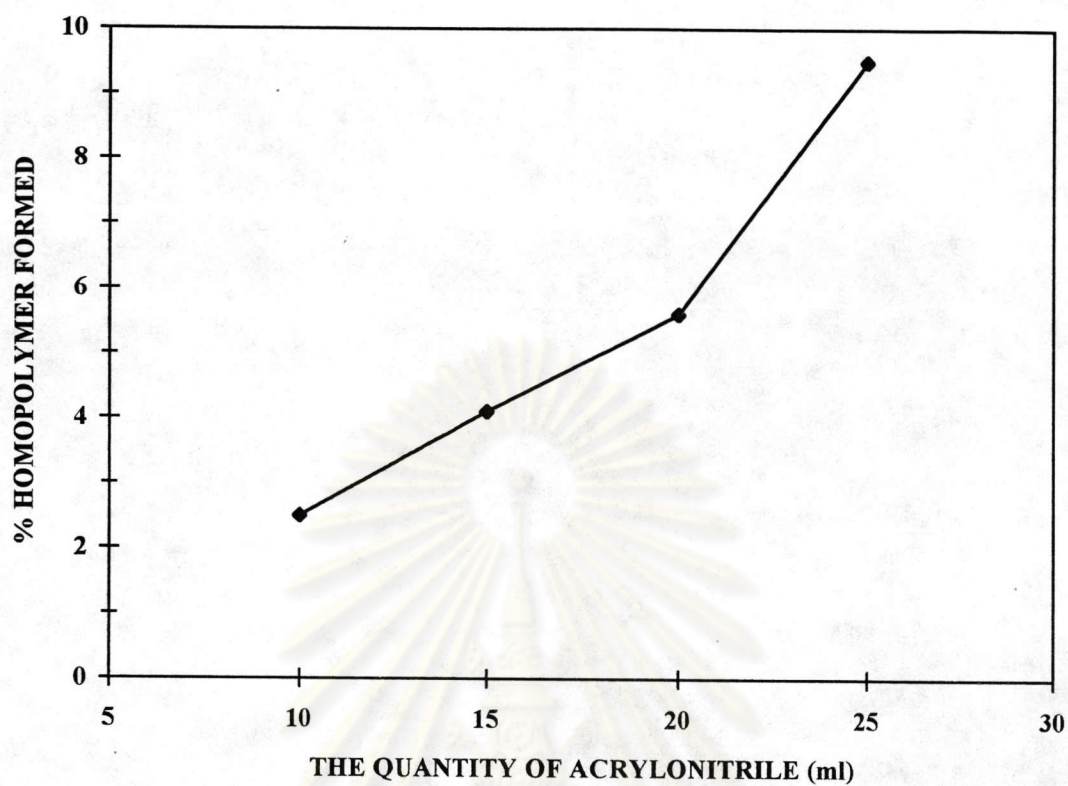
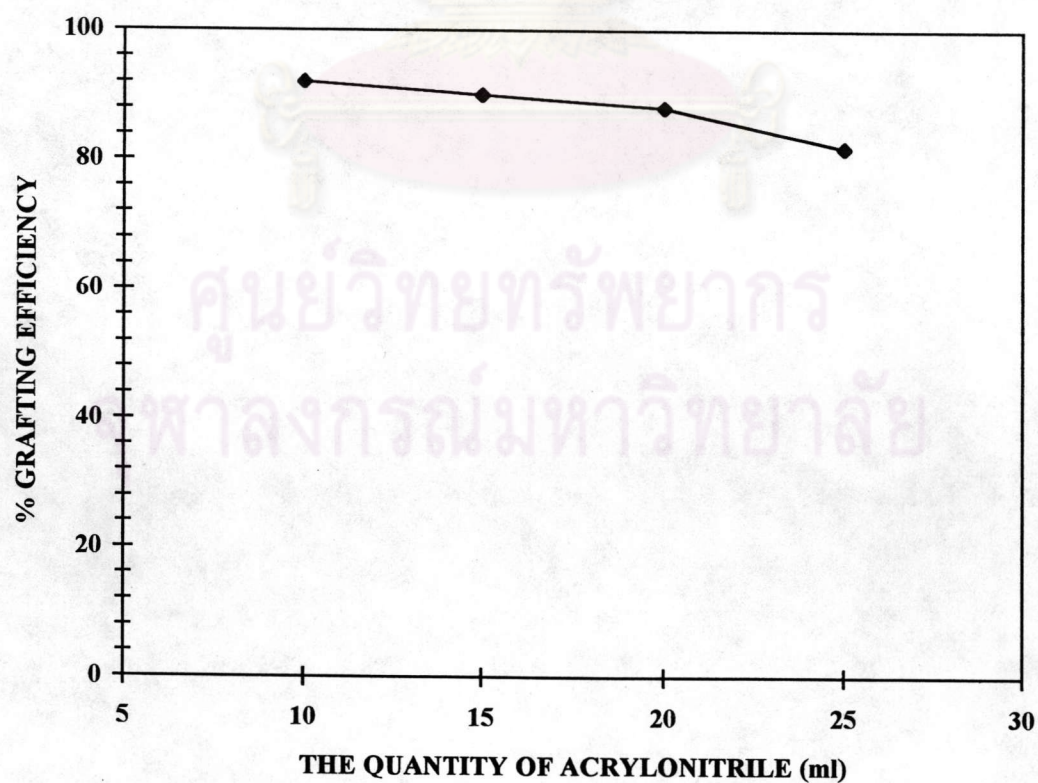Figure 4.22 Effect of the quantity of acrylonitrile on percent homopolymer

Figure 4.23 Effect of the quantity of acrylonitrile on grafting efficiency

quantity leading to higher amount of homopolymer at the initiation step, is possibly due to primary termination where an exessive amount of monomer was used to terminate the propagating radicals of homopolymer rather than the graft copolymer. In addition, the initiation rate can be monomer dependent that would directly alter the efficiency of the gamma rays (22).

6.3 Relationship between The Quantity of AN(ml) and Percent Conversion

The correlations between percent conversion of the monomer and the amount of monomer are shown in Table 4.16 and illustrated in Figure 4.24. It indicates a fixed relationship for this type of copolymerization. The linear relationship between starch-to-AN ratios and percent conversion is that the increasing amount of AN does not increase the conversion of the reaction significantly. This is the upper limit of total dose given that can eventually affect polymerizations. The limitation may come from the initiation step where the ionizing radiation cannot initiate any more free radicals than those radicals acquirable. If more doses were given to this system, the percent conversion might increase accordingly.

6.4 Relationship between The Quantity of AN(ml) and Percent Add-on

Figure 4.25 shows that the effect of the quantity of AN on percent add-on. The percent add-on was increased when increasing the quantity of AN. This result indicates that the increased AN produces the long grafted-PAN. As the quantity of monomer increases, homopolymer and graft copolymer also increase but not enough to highten percent conversion.
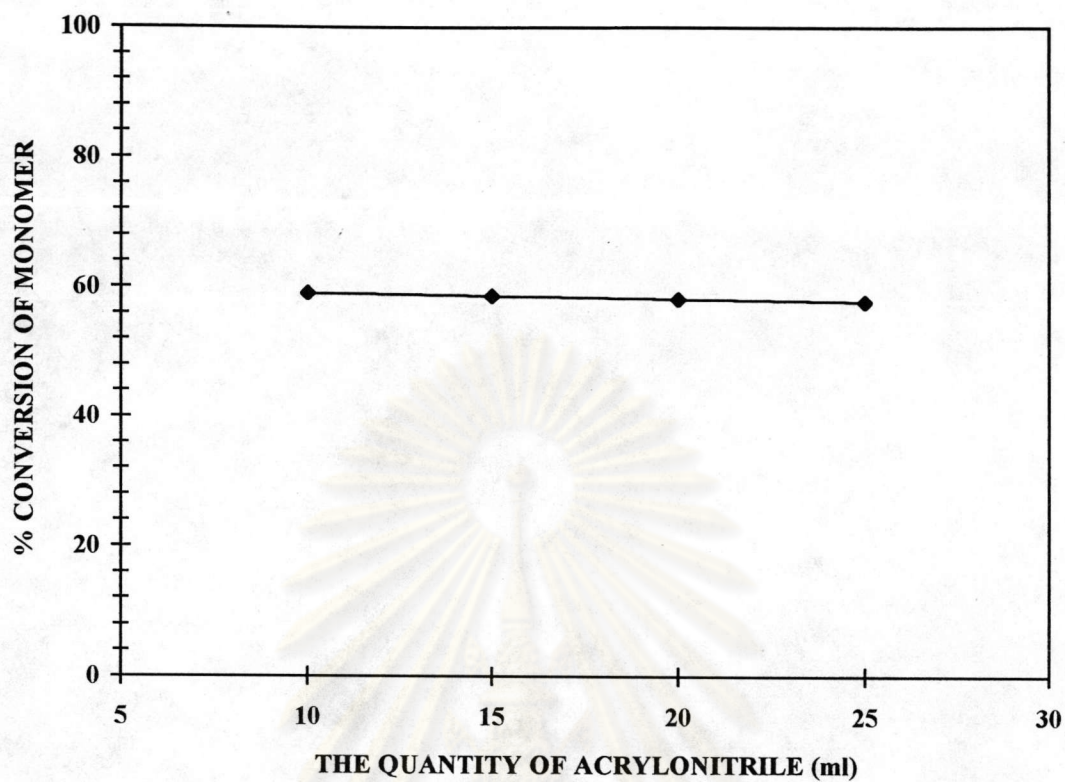
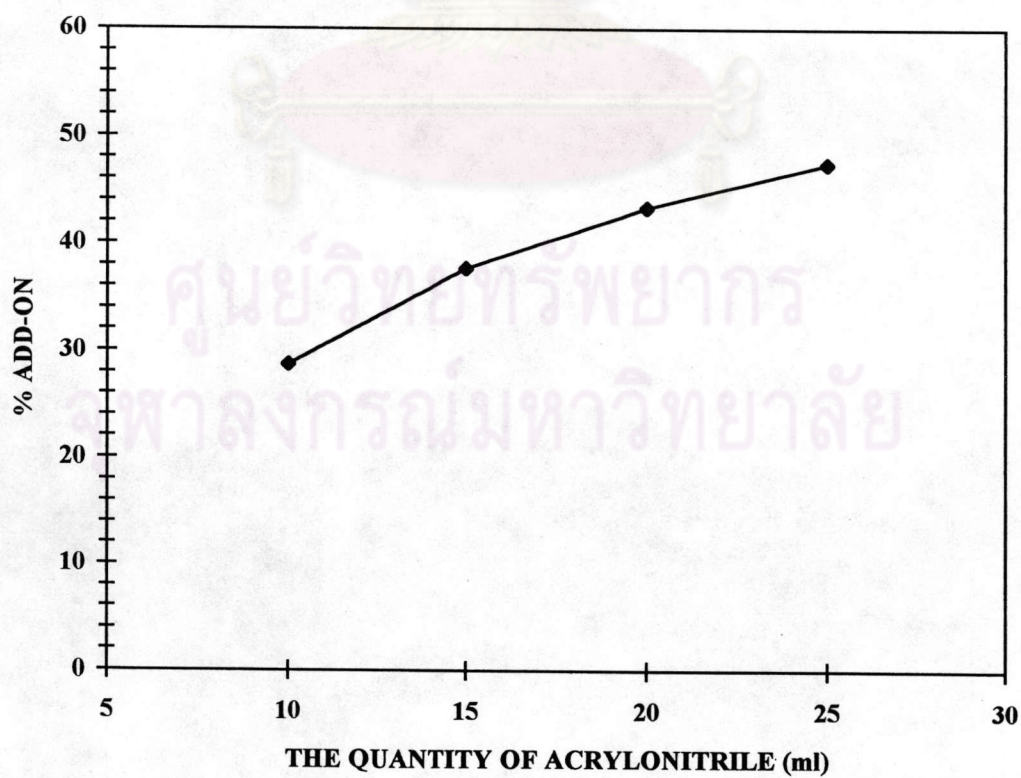Figure 4.24 Effect of the quantity of acrylonitrile on percent conversion

Figure 4.25 Effect of the quantity of acrylonitrile on percent add-on

6.5 Relationship between The Quantity of AN(ml) and Grafting Ratio

The effect of the quantity of AN on grafting ratio is also shown in Table 4.16 and Figure 4.26. It indicated that the grafted PAN/weight of starch still increased if more acrylonitrile was added. According to the definition of percent grafting ratio, the higher the number, the more grafted PANs were joint to the starch backbone. When the quantities of AN increase, the grafted PANs increase. Thus, percent grafting ratio is high.
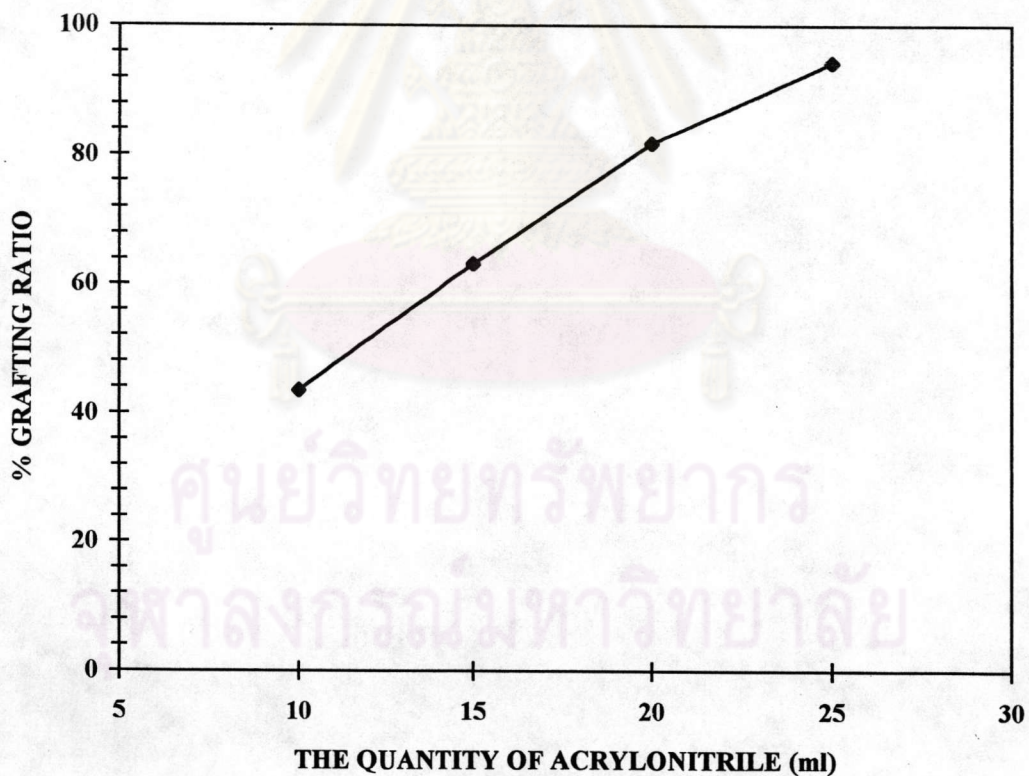

Figure 4.26 Effect of the quantity of acrylonitrile on grafting ratio

6.6 <u>Relationship between The Quantity of AN(ml) and Viscosity Average Molecular Weight and Grafting Frequency</u>

The effect of the quantity of acrylonitrile on the viscosity average molecular weight ($\overline{M}_v$) and the grafating frequency is given in Table 4.17.

a) Relationship between The Quantity of AN(ml) and Viscosity Average Molecular Weight

Figure 4.27 and Table 4.17 illustrate the effect of the quantity of AN (ml) on the molecular weight ($\overline{M}_v$) of grafted PAN. When increasing the quantity of acrylonitrile from 10 to 25 ml, the $\overline{M}_v$ of grafted PAN increased from 73,700 to 150,500 respectively. Under the low monomer quantity, the low ratio of propagation probably results in more termination reactions thus keeping the $\overline{M}_v$ of the PAN chains low (24). As more AN were present in the reaction mixture, there were more probability that AN could be grafted on the starch backbone. This results in increasing of the $\overline{M}_v$ of grafted chain.

Table 4.17 Effect of The Quantity of AN(ml) on the Viscosity Average Molecular Weight and the Grafting Frequency

AN(ml)	Molecular weight ($\overline{M}_v$)	Grafting Frequency (AGU/chain)
10	73,700	1,130
15	104,000	1,065
20	129,400	1,047
25	150,500	1,033

b) Relationship between the quantity of AN (ml) and Grafting Frequency

Figure 4.28 shows the effect of quantity of AN on grafting frequency. The less the AN quantity, the less reaction between AN and starch. Consequently, The number of AGUs/chain is higher. The number of AGUs/chain is almost the same at the AN of 20 and 25 ml. It may be the result from steric effect of grafted PAN chain. The high quantity of the monomer probably favours a rapid initial buildup of PAN side chains that in turn might hinder the movement of the monomer to other active sites on the carbohydrate backbone thus favouring the addition of the monomer to the growing end of the PAN rather than to another active site on the polymer backbone (24).
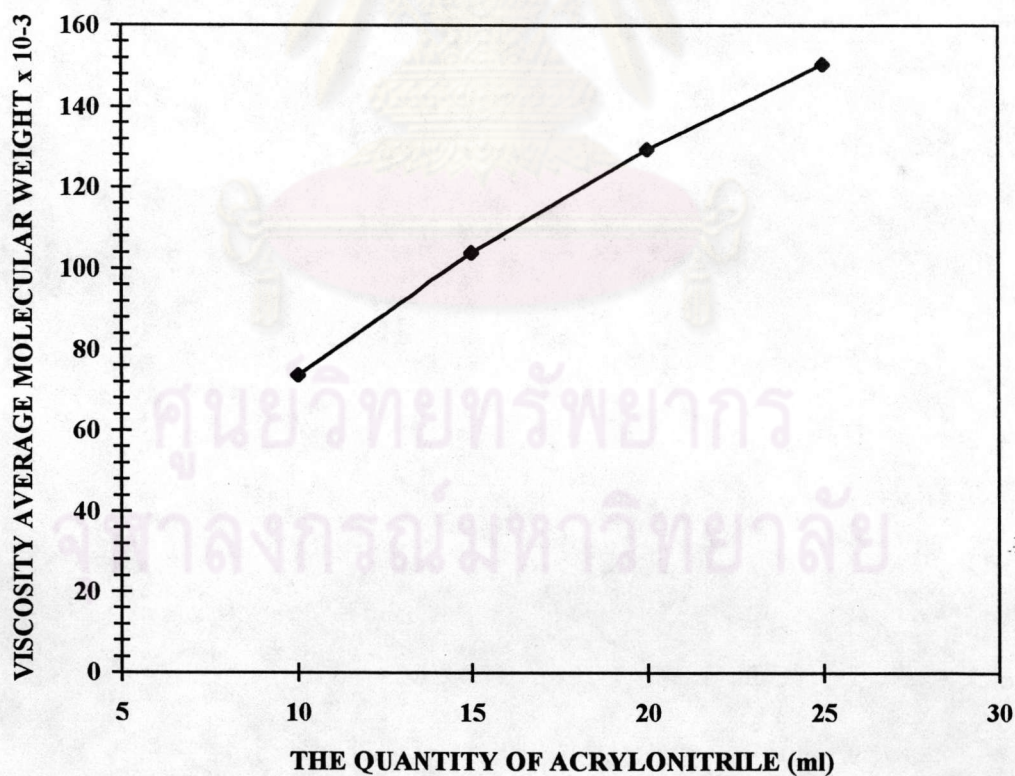

Figure 4.27 Effect of the quantity of acrylonitrile on viscosity average molecular weight
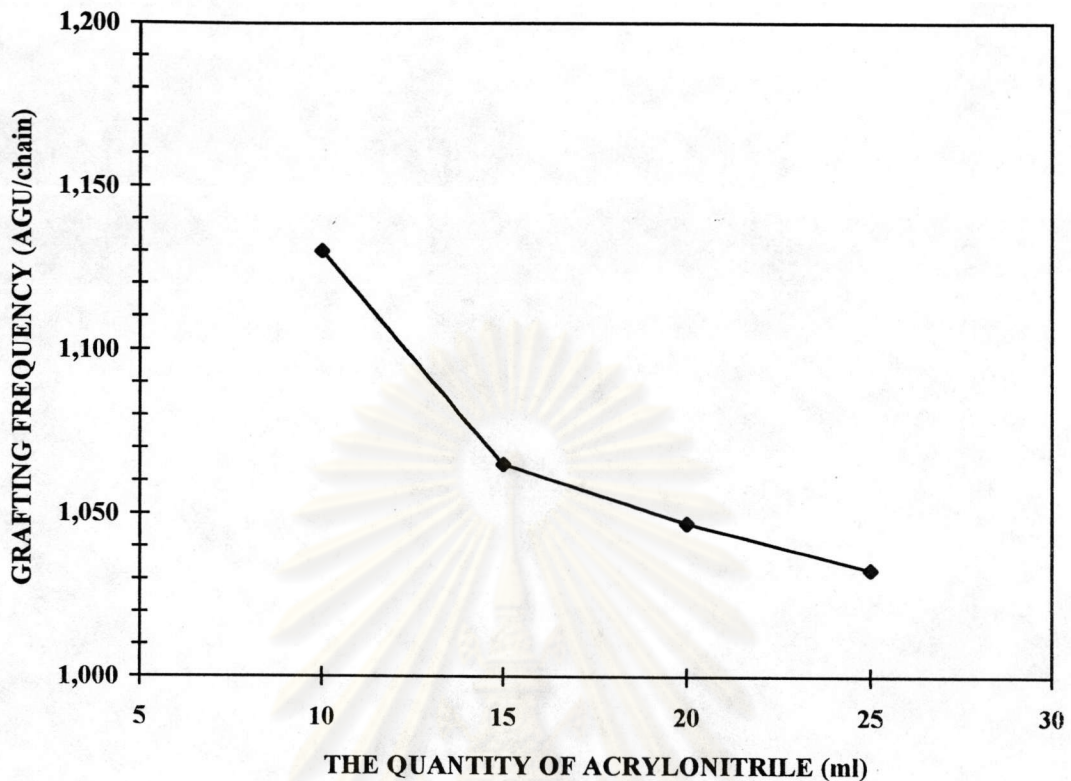
Figure 4.28 Effect of the quantity of acrylonitrile on grafting frequency

6.7 Relationship between The Quantity of AN (ml) and Water Absorption

The effect of the quantity of AN (ml) on the water absorption of the saponified starch-g-PAN in deionized distilled water is tabulated in Table 4.18 and shown in Figure 4.29.

The experimental data shows that the highest water absorption occured at the quantitiy of AN about 20 ml. The swelling is considered to be caused by osmotic pressure differential resulting from a difference in concentration of mobile ions between the interior of the gel and the external solution (34). The concentration of mobile K^+ ions in the polymer gel, resulting from the saponification step,   is higher than those in deionized water which comprises only hydrogen and oxygen atoms.

Table 4.18 Effect of the Quantity of AN on Water Absorption in
Deionized Distilled Water

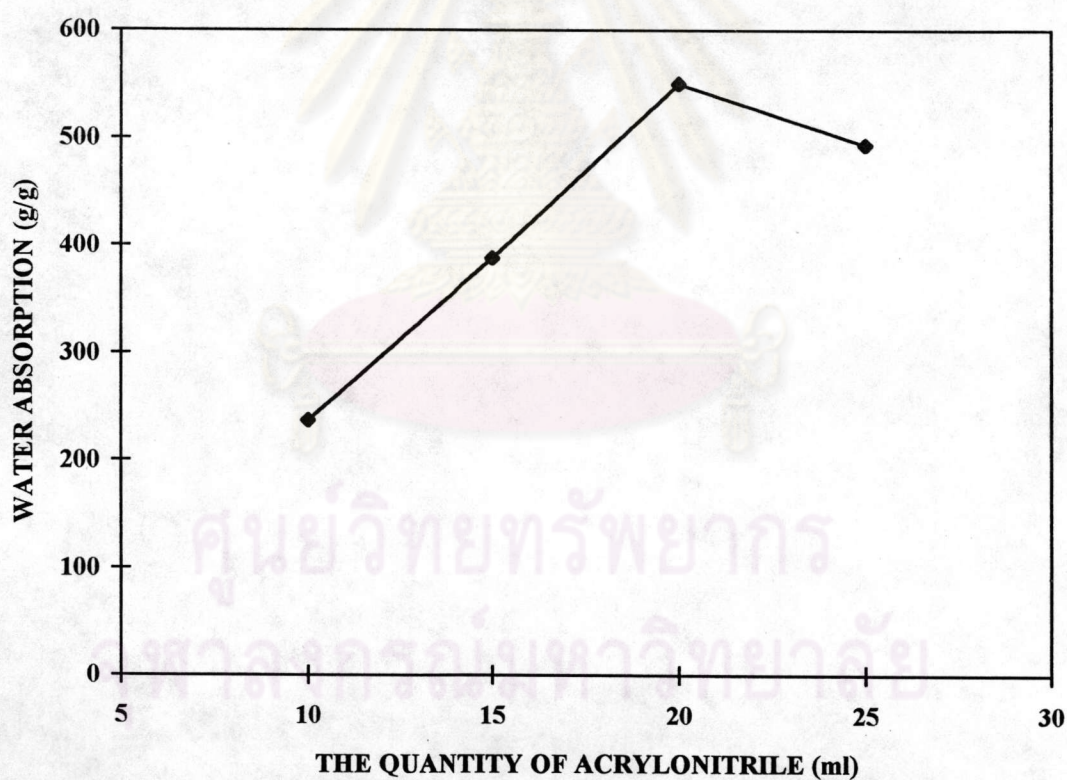| AN (ml)	Water absorption in deionized distillated water (g/g)
10	237
15	388
20	550
25	493

Figure 4.29 Effect of the quantity of acrylonitrile on water absorption
in deionized distilled water

As the ionic groups cannot move out of the gel, the solution within the gel is regarded as separated from the external solution by a semipermeable membrane which confines to the potassium carboxylate and carboxamide groups, but gives passages of water. The gel swells as a result of the difference in ion concentrations. Swelling continues until the osmotic pressure differential is equal to the resistance to further expansion, i.e., when the ion concentration between inside and outside the gel has reached equilibrium.

In conclusion, the effect of water absorption depends on the frequency of interposition of the grafted polymer chains on the starch backbone, and the nature of the grafted polymer, which means the amount of grafting chain or acrylonitrile and its molecular weight are some of the determining factors for water absorption.

6.8 Effect of NaCl Solutions on Water Absorption

The effect of NaCl solutions at the concentrations of 0.1, 0.5, 1.0, and 2.0% w/v on the water absorption is clearly illustrated in Table 4.19 and Figure 4.30. The water absorption efficiency of the saponified starch-g-polyacrylonitrile is very dependent on the ion concentration. Indeed, the effect of NaCl at different concentrations shows a dramatic decrease in water absorption in the presence of ions.

Table 4.19 Effect of NaCl Concentrations on Water Absorption

AN(ml)	Water Absorption in g/g			
	0.1%[a]	0.5%[b]	1.0%[c]	2.0%[d]
10	91	65	52	38
15	99	71	57	40
20	120	85	60	47
25	108	78	62	43

[a] $[Na^+] = [Cl^-] = 0.017$, $[Na^+] + [Cl^-] = 0.034$ mole-ion/l

[b] $[Na^+] = [Cl^-] = 0.085$, $[Na^+] + [Cl^-] = 0.170$ mole-ion/l

[c] $[Na^+] = [Cl^-] = 0.171$, $[Na^+] + [Cl^-] = 0.342$ mole-ion/l

[d] $[Na^+] = [Cl^-] = 0.342$, $[Na^+] + [Cl^-] = 0.684$ mole-ion/l

The effect of salt concentration on the water retention values is best explained in termes of the swelling of modified starch gels containing anionic groups. This treament was proposed by Grignon and Scallman (34) in terms of swelling of such gels as described above. Briefly this approach may be summarized in the following way:

The ions attached to the macromolecular network in the gel are immobile and are considered to be saparated from the external solution by a semipermeable membrane, which confines the immobile ions, but gives passage to water and all simple ions. The excess concentration of mobile ions in the gel phase is calculated using Donnan's equilibrium model. This excess concentration is directly proportional to osmotic pressure differential, and this, in turn, is assumed to be directly proportional to degree of swelling, i.e., to the water absorption itself (35).

In this case the graft copolymer is present as the anion of potassium salt (polycarboxylate) and polycarboxamide, which are assumed to be a strong electrolyte. When saponified starch graft copolymer was placed in
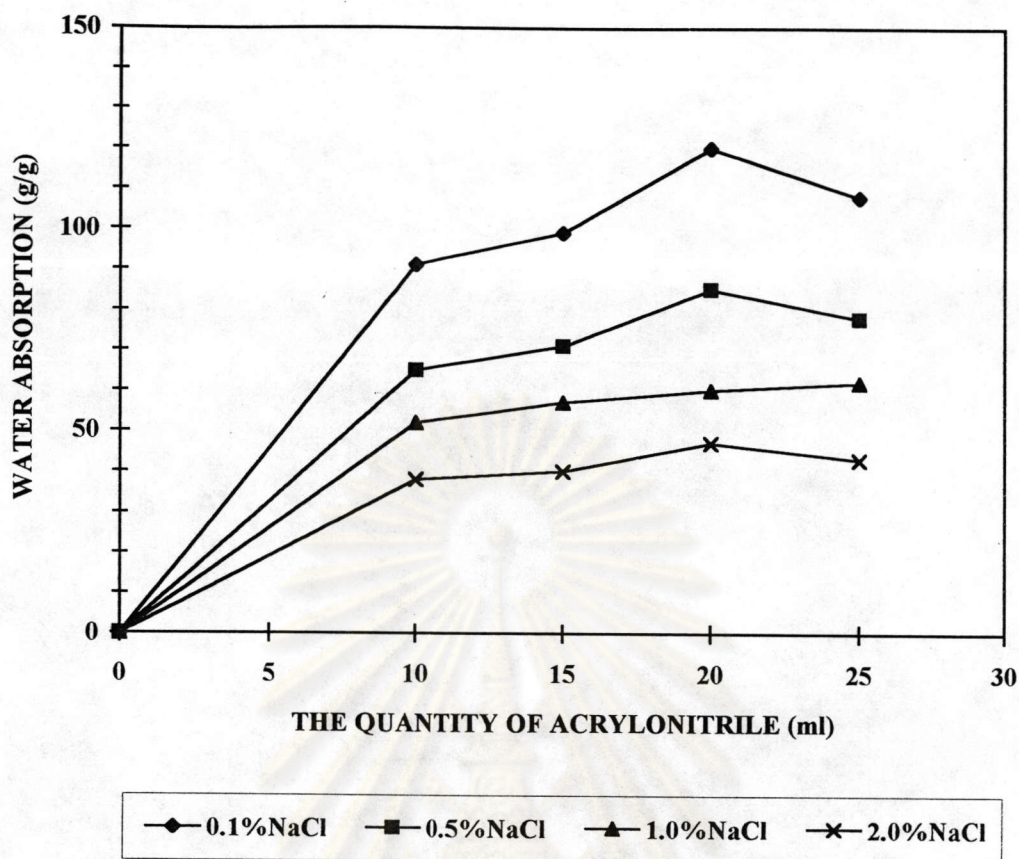
Figure 4.30 Water absorption of saponified starch-g-PAN in NaCl
solutions of 0.1, 0.5, 1.0, and 2.0% w/v.

NaCl solutions, at the surface of this material the behavior as semipermeable membrane exists. To maintain electrical neutrality on the both sizes of the membrane, Na^+ and Cl^- ions have diffused through the membrane from external solution to the interior of gels. The amount of NaCl diffused from external solution to the interior of gel is inversely proportional to the concentration of non-diffusible ion, polycarboxylate. This unequal distribution of the diffusible ions (Na^+ and Cl^-) in the two compartments is the result of the Donnan effect (36), assume that the saponified starch graft copolymer has the same behavior as the sodium salt of protein.

The osmotic pressure of this system is now determined by the difference between the number of particles in the external solution and that in the interior of the gel. Assume that K^+ ions in the interior of the gel have the same concentration (mole-ion/l) as that of polycarboxylate.

Then,

$$\pi \quad = \quad \frac{2a^2 + 2ab}{a + 2b} \quad RT \tag{4.5}$$

Where,

π : osmotic pressure, atm

a : concentration of polycarboxylate and K^+ ions in the interior of the gel, mole-ion-l^{-1}

b : concentration of Na^+ and Cl^- ions in the external solution, mole-ion-l^{-1}

R : gas constant, 8.314 J K^{-1}mol^{-1}

T : temperature, K

According to eq. 4.5 the concentration of salt solution increases, the osmotic pressure of this system would then decrease. The more ions are present, the less water is absorbed. In soil environment, a similar effect is expected as soils contain various types of ions and plant nutrients. The use of fertilizer in agriculture, horticulture, and arboriculture also has such an effect, a reduction in water absorption. In order to compensate for the decrease in water intake, the use of more superabsorbent polymer is therefore necessary.

6.9 Effect of MgCl₂ Solutions on Water Absorption.

The water absorption of the saponified starch-g-polyacrylonitrile copolymers in 0.1, 0.5, 1.0 and 2.0% w/v of magnesium chloride solutions is given in Table 4.20 and Figure 4.31.

On observing the case of $MgCl_2$, the water absorption decreased even more with increasing magnesium chloride concentrations. As a consequence, the absorption with $MgCl_2$ solution is much less than does NaCl. Here the highest water intake of $MgCl_2$ solution is less than 90 g/g, while that of NaCl the value obtained is 140 g/g.

Table 4.20 Effect of Different $MgCl_2$ Concentrations on Water Absorption

AN(ml)	Water Absorption in g/g			
	$0.1\%^a$	$0.5\%^b$	$1.0\%^c$	$2.0\%^d$
10	42	27	25	24
15	53	31	28	26
20	90	44	37	30
25	86	42	34	29

[a] $[Mg^{2+}] = 0.010$, $[Cl^-] = 0.020$, $[Mg^{2+}] + [Cl^-] = 0.030$ mole-ion/l

[b] $[Mg^{2+}] = 0.052$, $[Cl^-] = 0.105$, $[Mg^{2+}] + [Cl^-] = 0.157$ mole-ion/l

[c] $[Mg^{2+}] = 0.105$, $[Cl^-] = 0.210$, $[Mg^{2+}] + [Cl^-] = 0.315$ mole-ion/l

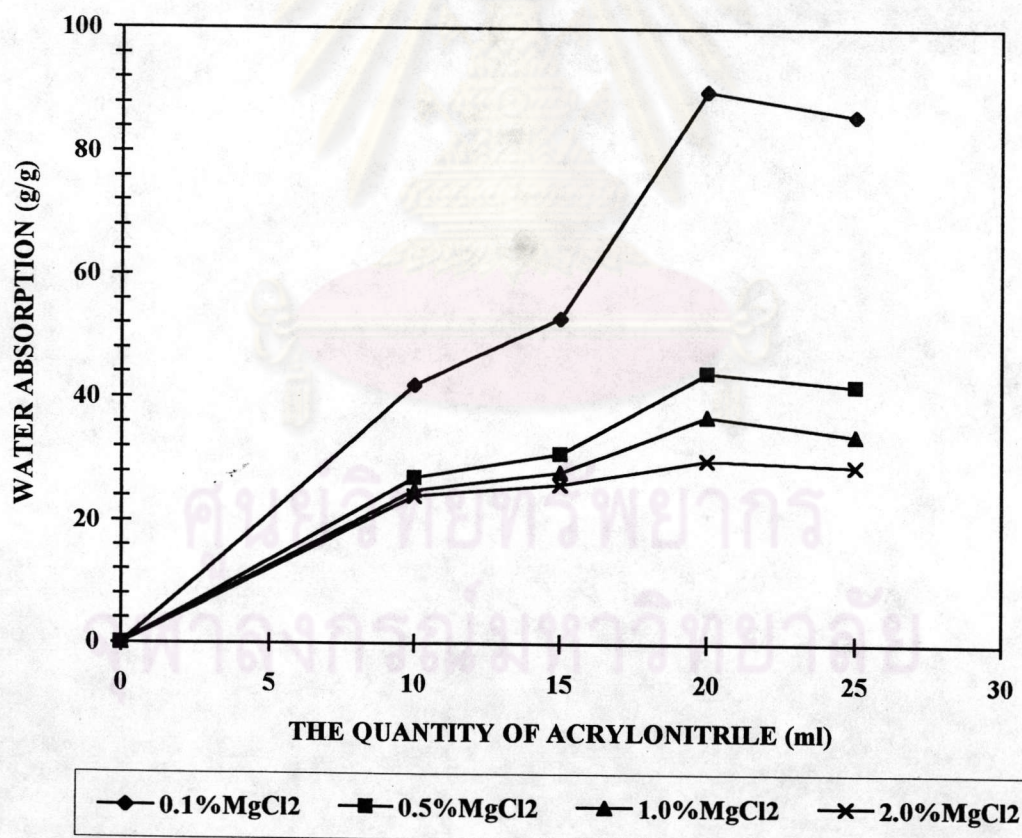[d] $[Mg^{2+}] = 0.210$, $[Cl^-] = 0.420$, $[Mg^{2+}] + [Cl^-] = 0.630$ mole-ion/l

Figure 4.31 Water absorption of saponified starch-g-PAN in $MgCl_2$ solutions of 0.1, 0.5, 1.0, and 2.0% w/v.

The water absorption of the starch-based superabsorbent in deionized distilled water as compared to the water absorptions of 0.1% w/v of NaCl and $MgCl_2$ is shown in Figure 4.32. At the concentration of 0.1% w/v of NaCl and $MgCl_2$, both Na^+ and Mg^{2+} have ion concentrations of 0.034 and 0.030 mole-ion/l respectively. The figure indicates decrease in water absorption with ions, especially divalent ions. It is the result of the osmotic pressure differential between the internal solution in the gel and external solution due to the different ion types (37). The water intake by the gel reduced the osmotic pressure until an ion concentration equilibrium was reached.
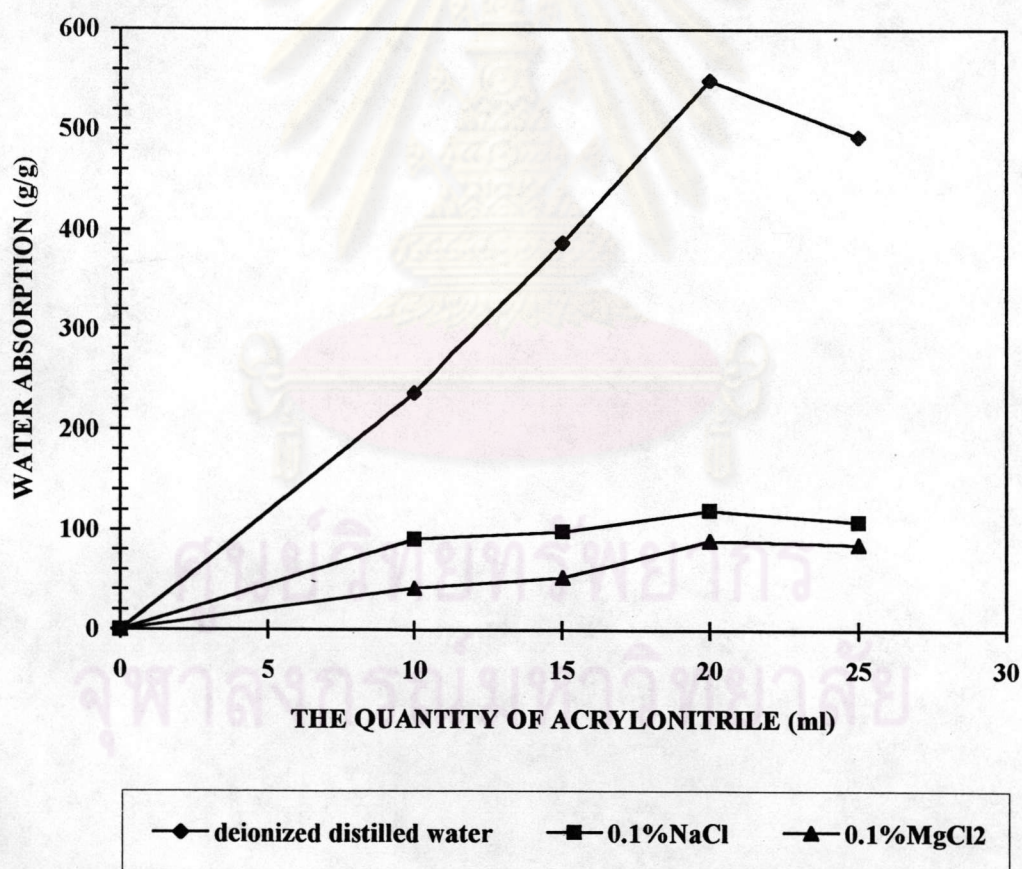

Figure 4.32 Comparision of water absorption of HSPAN in deionized distilled water and 0.1% w/v of NaCl and $MgCl_2$

6.10 Effect of $K_3PO_4 \cdot 3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ Solutions on Water Absorption

The water absorption of the graft copolymer in the presence of $K_3PO_4 \cdot 3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ is given in Table 4.21 and Figure 4.33. All of these salts have the concentration of 0.9% w/w.

The result in the table 4.21 shows that the water absorption decreases in relation to that of deionized water. The absorbency of the saponified starch-g-PAN is presumably dependent upon the following three factors:

Table 4.21 Effect of $K_3PO_4 \cdot 3H_2O$, KCl, NH_4Cl, and $(NH_4)_2HPO_4$ with Identical Concentration of 0.9% w/w on the Water Absorption of the Saponified Starch-g-Polyacrylonitrile

AN(ml)	Water Absorption (g/g) in			
	$K_3PO_4 \cdot 3H_2O$[a]	KCl[b]	NH_4Cl[c]	$(NH_4)_2HPO_4$[d]
10	52	55	43	46
15	65	70	50	54
20	75	90	62	73
25	63	82	57	58

[a] $[K^+] = 0.101$, $[PO_4^{3-}] = 0.034$, $[K^+] + [PO_4^{3-}] = 0.135$ mole-ion/l

[b] $[K^+] = [Cl^-] = 0.121$, $[K^+] + [Cl^-] = 0.242$ mole-ion/l

[c] $[NH_4^+] = [Cl^-] = 0.168$, $[NH_4^+] + [Cl^-] = 0.336$ mole-ion/l

[d] $[NH_4^+] = 0.136$, $[HPO_4^{2-}] = 0.068$, $[NH_4^+] + [HPO_4^{2-}] = 0.204$ mole-ion/l

a) the osmotic pressure;

b) the molecular chain expansion resulting from repulsion between the electrolyte anions in the polymer chains;

c) the extent of crosslink affecting the degree of swelling of the polymer;

The absorbency (Q) can be expressed by the Flory's equation shown as following:

$$Q^{5/3} = [(i/2 \cdot V_u S^{*1/2})^2 + (1/2 - x_1)/v_1] (v_e/V_o) \qquad (4.6)$$
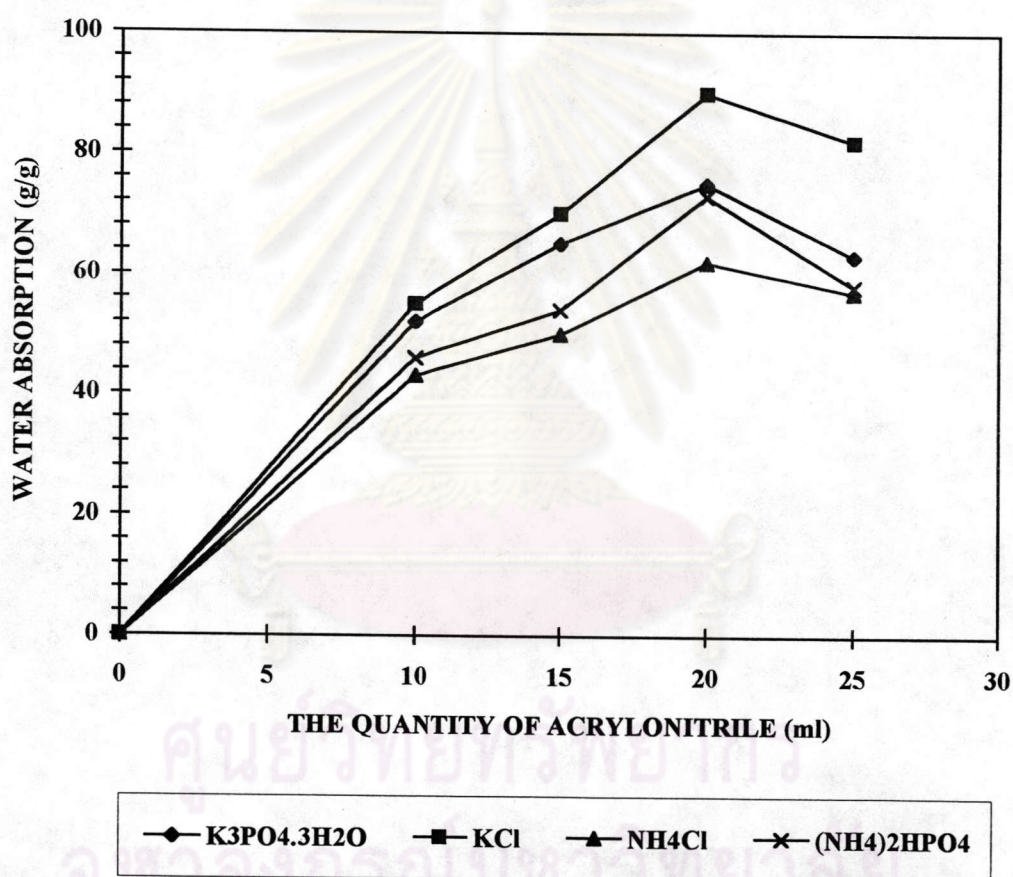

Figure 4.33 Water absorption of saponified starch-g-PAN in KCl, $K_3PO_4 \cdot 3H_2O$, NH_4Cl, and $(NH_4)_2HPO_4$ solutions of 0.9% w/w.

where,

        i : degree of ionization of polymer electrolyte

        S^* : ionic strength of salt solution added

$(1/2 - x_1)/v_1$: affinity between ionic network and
the absorbed water

V_u : molar volume of polymer repeating unit

v_e/V_o : crosslinking density

Figure 4.34 shows the relationships between the absorbency (Q) and the factors mentioned above (1).
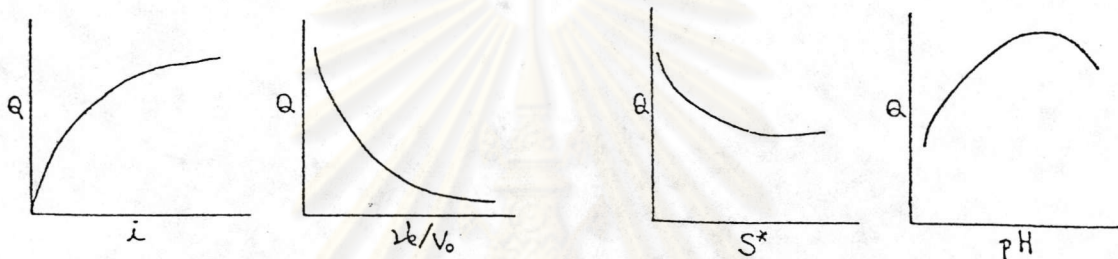

Figure 4.34 Relationship between swelling degree and ionization degree
of polymer electrolyte,   crosslinking density of polymer
network, ionic strength of salt solution,   and pH of polymer
solution.

The different water absorption in the solution of salts depends on the effect of osmotic pressure as described in eq. 4.5, ionic strength of salt solution, and other factors described in eq. 4.6: crosslinking density, molar volume of polymer repeating unit and the affinity of between the polymer network and the absorbed water.

6.11 Effect of Simulated Urine Solution on Water Absorption

The water absorptions of the graft copolymer in simulated urine solution and deionized distilled water are shown in Table 4.22.

Table 4.22 Effect of Simulated Urine on Water Absorption of the HSPAN

AN(ml)	Water Absorption (g/g) in	
	Simulated Urine[a]	Deionized Distilled Water
10	45	237
15	52	388
20	76	550
25	63	493

[a]$[Ca^{2+}] = 0.0058$, $[Cl^-] = 0.0116$, $[Ca^{2+}] + [Cl^-] = 0.0174$ mole-ion/l

$[Mg^{2+}] = [SO_4^{2-}] = 0.0046$, $[Mg^{2+}] + [SO_4^{2-}] = 0.0092$ mole-ion/l

$[Na^+] = [Cl^-] = 0.1400$, $[Na^+] + [Cl^-] = 0.2800$ mole-ion/l

The result in the above table shows that the water absorption decreases considerably in simulated urine solution in relation to that of deionized distilled water. It is attributed to the effects of salt concentrations in the solution, especially, the negative effect of the divalent cations, Ca^{2+} and Mg^{2+}. .

6.12 Water Absorption in Sand Alone and Sand with Saponified Starch-g-Polyacrylonitrile

In order to determine the water retention capacity in soil environment, the newly synthesized copolymer was tested by mixing it with sand with the particle size average larger than 100 mesh at the concentrations of 0.5, 1.0, 2.0, and 3.0%. The absorption data are given in Table 4.23 and illustrated in Figure 4.35 and the absorption of sand alone is 0.4 g/g. They clearly show that the water absorption in sand depends to a large extent, on the amount of polymer used. There is a linear relationship between water retention and polymer concentration, i.e. the concentration of the grafted copolymer increased, so did the was retention.

The absorption efficiency of the copolymer also plays an important role in water retention of sand. The water retention of sand mixed with HSPAN synthesized with different AN concentration is shown in Figure 4.36.

Table 4.23 Water Retention on Sand Mixed with Different Concentrations of Saponified Starch-g-Polyacrylonitrile

AN(ml)	Water Absorption, g/g, with the addition of polymer, %, to sand			
	0.5	1.0	2.0	3.0
10	141	144	146	178
15	173	192	201	224
20	303	317	372	431
25	240	252	271	315

7. Modification of Saponified Starch-g-PAN with Aluminium Chloride on Water Absorption and Wicking Time: Dependence on Drying Method

According to the results of the total dose of 3.5 kGy, aluminium foil covered the inner wall of the irradiated tube and nitric acid inclusion for graft copolymerization of AN onto cassava starch, the HSPAN have the maximum water absorption in deionized distilled water which is 550 times it dried weight.
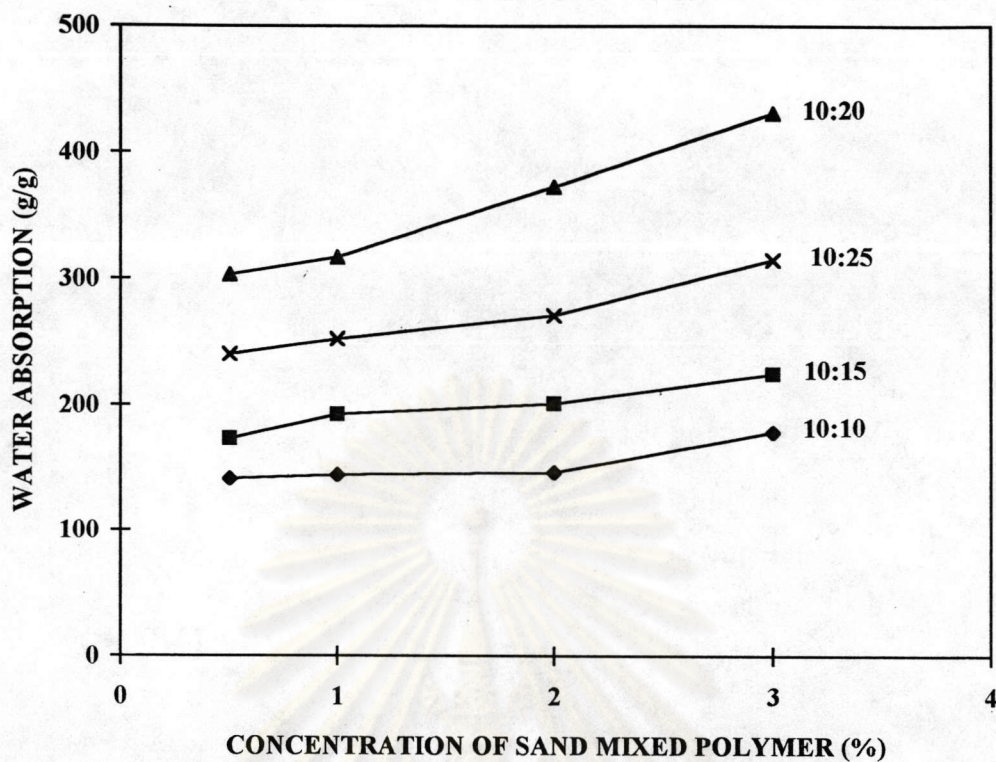
Figure 4.35 Water retention of sand mixed with saponified starch-g-PAN
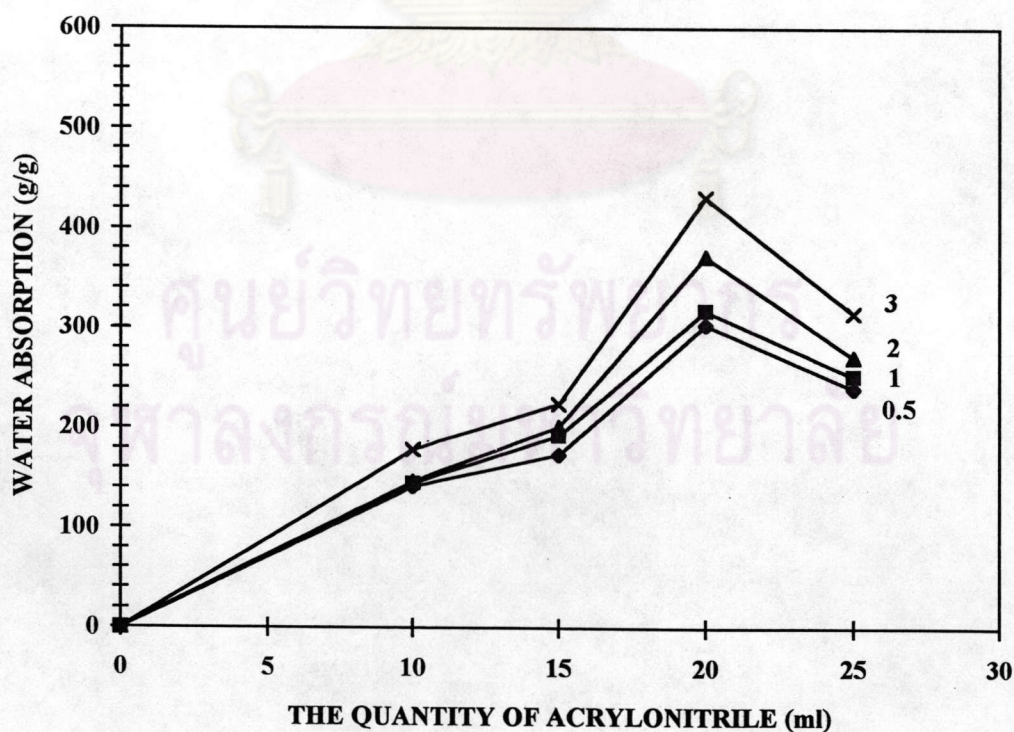with different AN concentration

Fig 4.36 Water retention of sand mixed with saponified starch-g-PAN
synthesized with different AN concentration

Table 4.24 The water absorption and wicking time of the HSPAN
depended on the quantity $AlCl_3 \cdot 6H_2O$ and drying method.

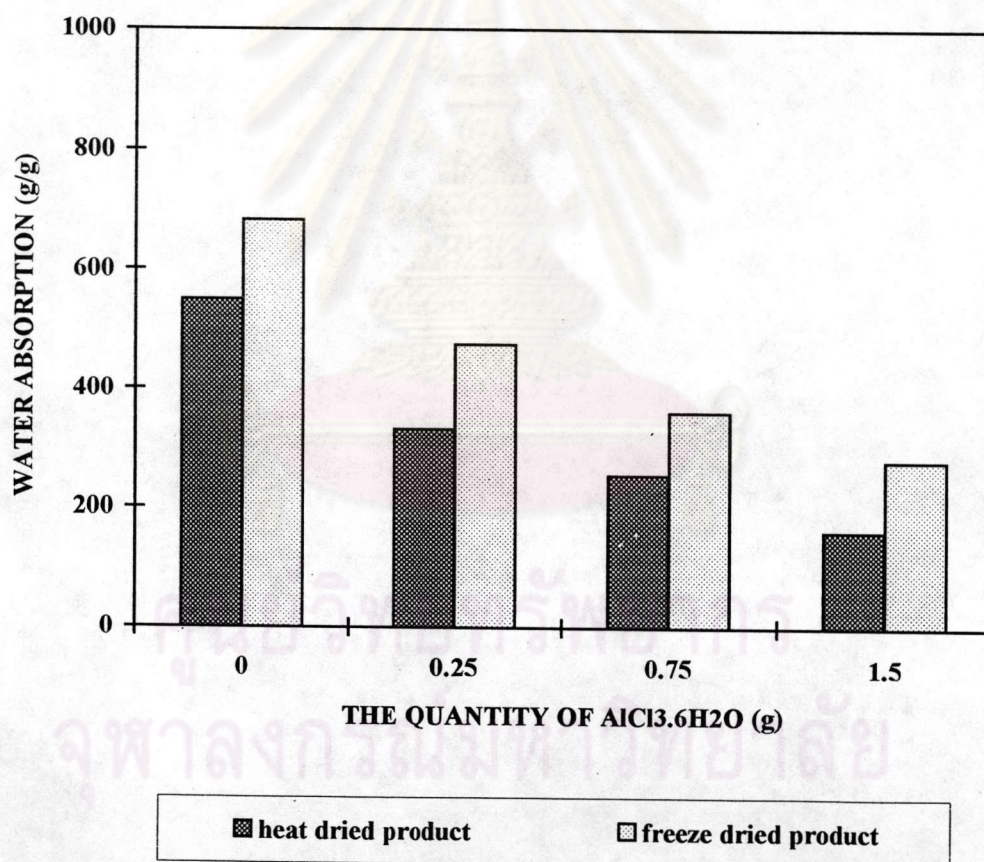| $AlCl_3 \cdot 6H_2O$	Water Absorption (g/g)		wicking
(g)	heat dried	freeze dried	time (min)
0(control)	550	682	15.30
0.25	332	475	7.40
0.75	255	360	1.20
1.25	160	278	0.30

Figure 4.37 Water absorption of the saponified starch-g-PAN modified
with the different quantities of aluminium trichloride and
drying methods

In Table 4.24 the water absorption and wicking time of the absorbent polymer are shown. Drying method has a strong influence on water absorption. Heat drying method gives the product with less water absorption than freeze drying method because of the induced crosslinking reaction during drying. The crosslinks between the grafted PAN caused by the high temperature lead to a decline in the water absorbency (38).

The effects of aluminium trichloride hexahydrate on water absorption and wicking time are shown in Table 4.24 and Figure 4.36. It indicates that aluminium ions render the HSPAN with an enhanced degree of wicking (absorption rapidly) and reduces the water absorption of the product. This phenomenone was explained by Elmquist (15) that the HSPAN was surface treated with aluminium ions, which reacted with the carboxyl groups of the HSPAN to form a product with a linkage density at the particle surface greater than the linkage density in the particle interior. The imbalance forces between the surface and the inner of the gel cause the equilibrium osmotic pressure to be reached sooner, therefore, the extent of water absorption is reduced.