

## Chapter 3

### Results and Discussion

#### 3.1 Definitions

The definitions of terms and grafting parameters are the same as used by previous investigators [8, 19-23].

The structure of a starch-g-PAN is as shown schematically in Figure 3.1, where AGU represents a glucopyranosyl unit, and M the monomer used in the graft copolymerization reaction. Starch concentrations, expressed in moles, refer to mole of AGU and have been calculated from a molecular weight of 162.

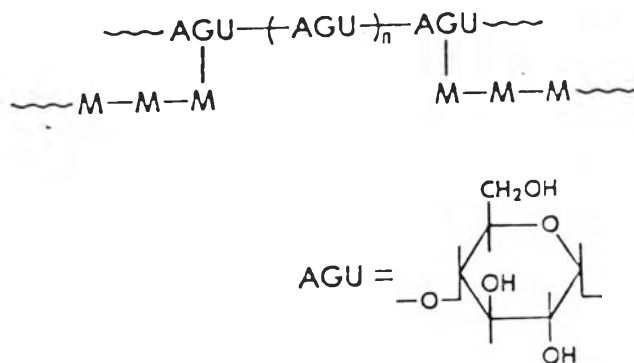


Figure 3.1 Schematic representation of a starch graft copolymer.

3.1.1 Percent add-on is referred to as the percent of synthetic polymer in the graft copolymer and is determined as follows:

$$\text{Percent add-on} = \frac{\text{Polymer in grafts}}{\text{Total weight of grafted sample}} \times 100$$

3.1.2 Grafting frequency is expressed as the average number of AGU separating each grafted branch and is easily calculated from the percent add-on and the  $\overline{M}_v$  of the copolymer:

$$\text{Grafting frequency (AGU/chain)} = \frac{(100 - \% \text{ add-on}) \times \overline{M}_v}{\% \text{ add-on} \times 162}$$

3.1.3 Grafting efficiency is a term often used to describe graft copolymerization reactions and is defined as the percentage of the total synthetic polymer formed that has been grafted to starch. For example, if half of the synthetic polymer produced in a graft copolymerization was an ungrafted homopolymer while the other half was chemically attached to starch, the grafting efficiency would be 50%. High grafting efficiencies are desirable since a polymerization of low grafting efficiency would afford mainly a physical mixture of starch and homopolymer. The grafting efficiency can be calculated as follows:

$$\text{Grafting efficiency (\%)} = 100 - \text{Homopolymer formed}$$

### 3.2 Grafting of acrylonitrile onto starch gelatinized at 65°C

Rånby and coworkers [20-23] studied the grafting of acrylonitrile with granular and gelatinized starch, and found that the efficiency of the grafting reaction was higher with gelatinized starch than with granular one. They explained that when gelatinized starch is used as a substrate, the accessibility of starch for grafting is enhanced, which will increase conversion. Regarding the MW of the resulting starch-g-PAN between granular and gelatinized starch, the latter had a MW up to eight times higher than the former. A higher MW of the graft copolymer has shown to give a higher water absorption [22]. In view of these findings, we chose to use gelatinized starch rather than the granular one. The pretreatment temperatures were 65°C and 80°C, and kept for one hr.

As emphasized in the Introduction Chapter, the initiation mechanism of vinyl monomers onto starch primarily involves the cleavage of glycol groups of the anhydroglucose units in amylose and amylopectin. The rate determining step in the glycol cleavage reaction appears to be the dissociation of the glycol-Mn<sup>3+</sup> complex. The overall glycol cleaving rate is governed by the concentration of Mn<sup>3+</sup>, the amount of sulphuric acid used and the glycol concentration [20].

Mehrotra and Rånby [20-23] have also studied the effect of reaction condition on the grafting. They found that, by varying the initiator concentration of  $Mn^{3+}$  from 0.15 mmole/L to 1.0 mmole/L, the % add-on as well as grafting efficiency increased dramatically, but from 1.0 mmole/L to 3.0 mmole/L the % add-on leveled off. In both cases, the sulphuric acid concentration was kept at 85.8 mmole/L. Grafting occurred readily even at a  $H_2SO_4$  concentration as low as 10 mmole/L. The grafting efficiency and the values of % add-on were high and showed only a slight variation with acidity. But at higher  $H_2SO_4$  concentration, however, the average MW of grafted chain decreased and reflected the more frequent grafts obtained [22]. Therefore in this study the reaction conditions were kept constant at 1 mmole/L of  $Mn^{3+}$  concentration and 85.8 mmole/L of  $H_2SO_4$  concentration.

### 3.2.1 IR analysis

Figures 3.2 - 3.5 show respectively the IR spectra of cassava starch, the starting material; the reaction product after grafting; the starch-g-PAN after DMF extraction; and the starch-g-PAN after saponification with KOH.

After the grafting reaction of acrylonitrile onto starch, a sharp peak occurred at  $2,243\text{ cm}^{-1}$  representing the stretching absorption band of the CN group [31]. This peak slightly decreased after DMF extraction of

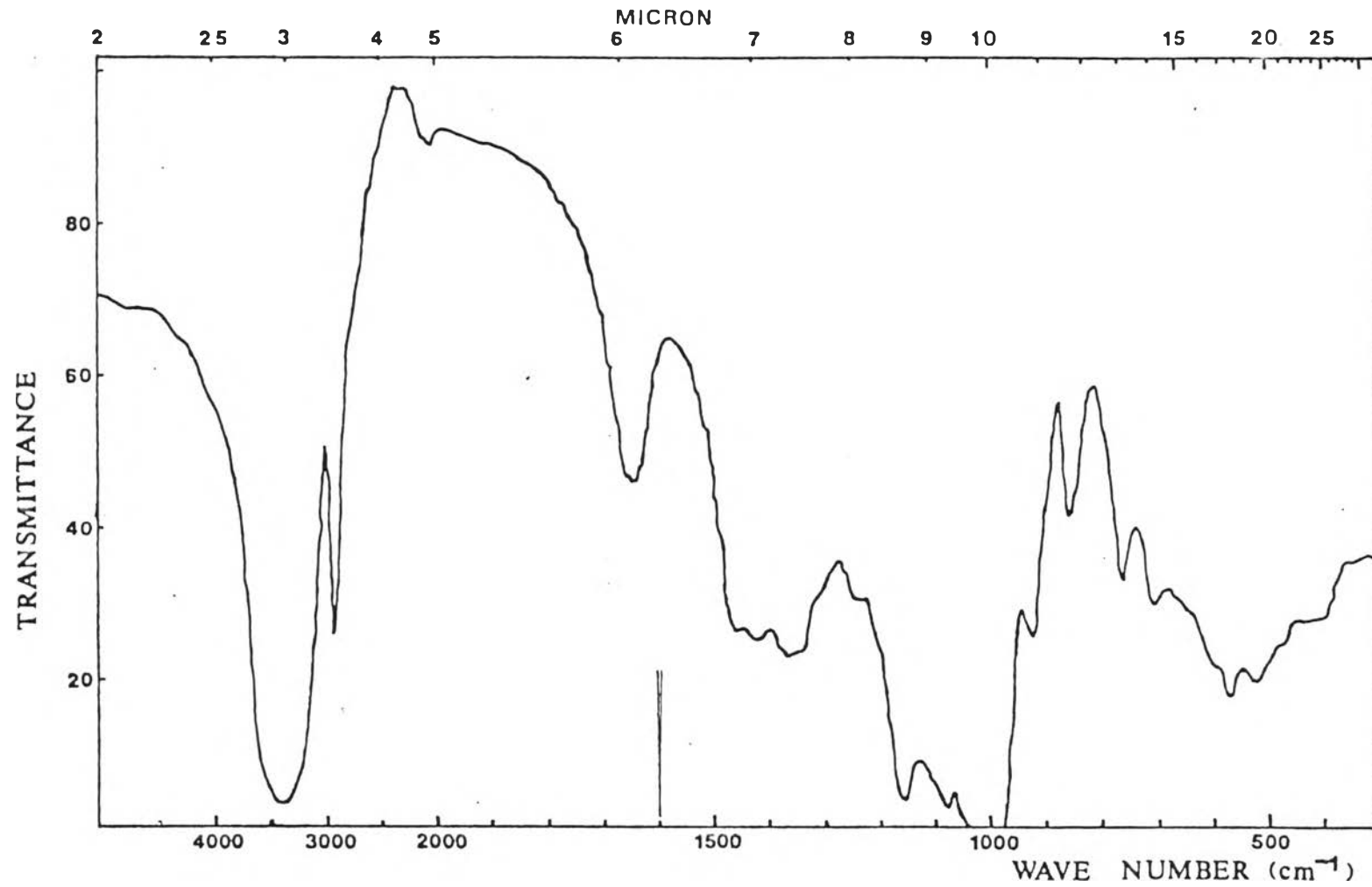


Figure 3.2 IR spectrum of cassava starch

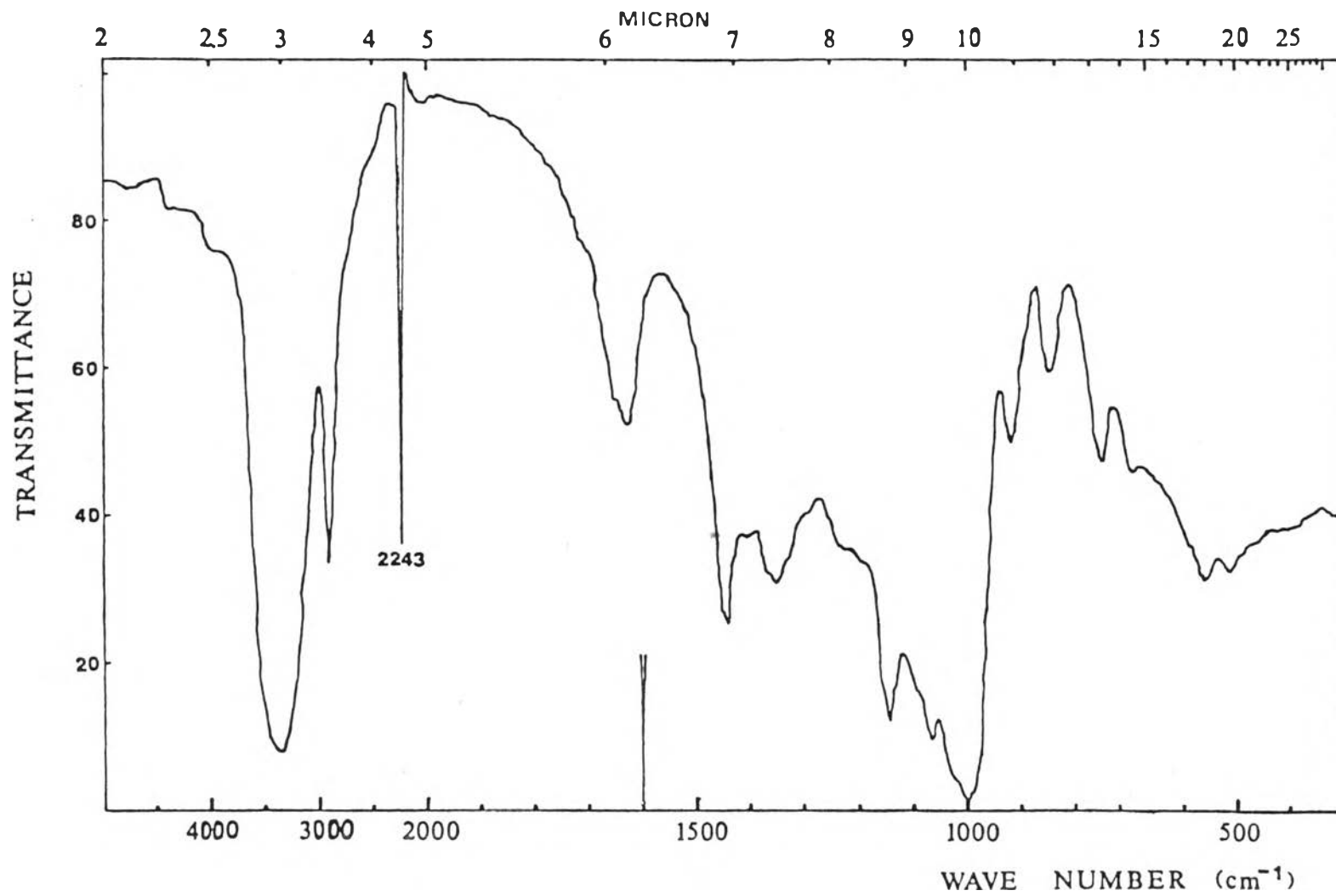


Figure 3.3 IR spectrum of starch-g-PAN

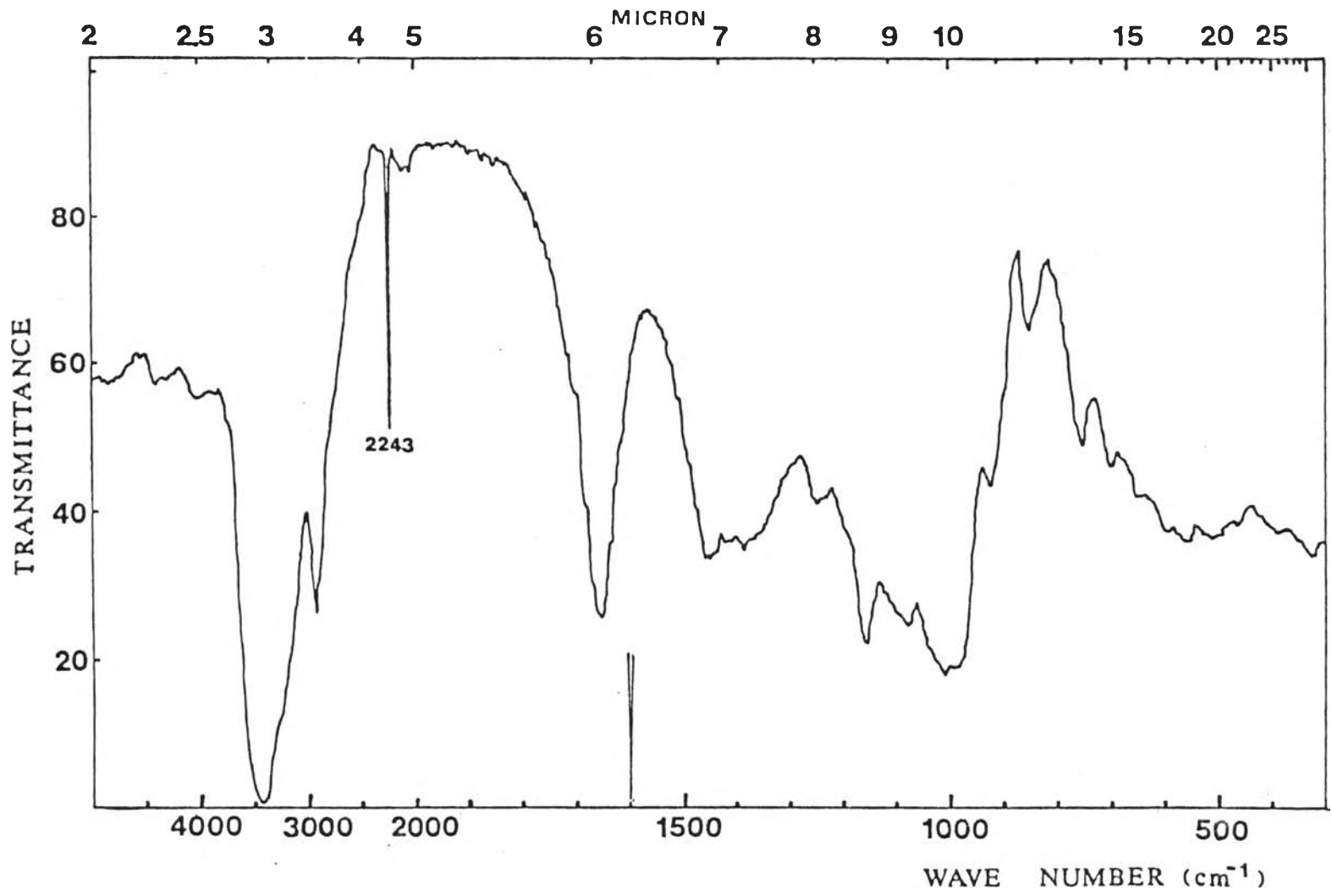


Figure 3.4 IR spectrum of starch-g-PAN after DMF extraction

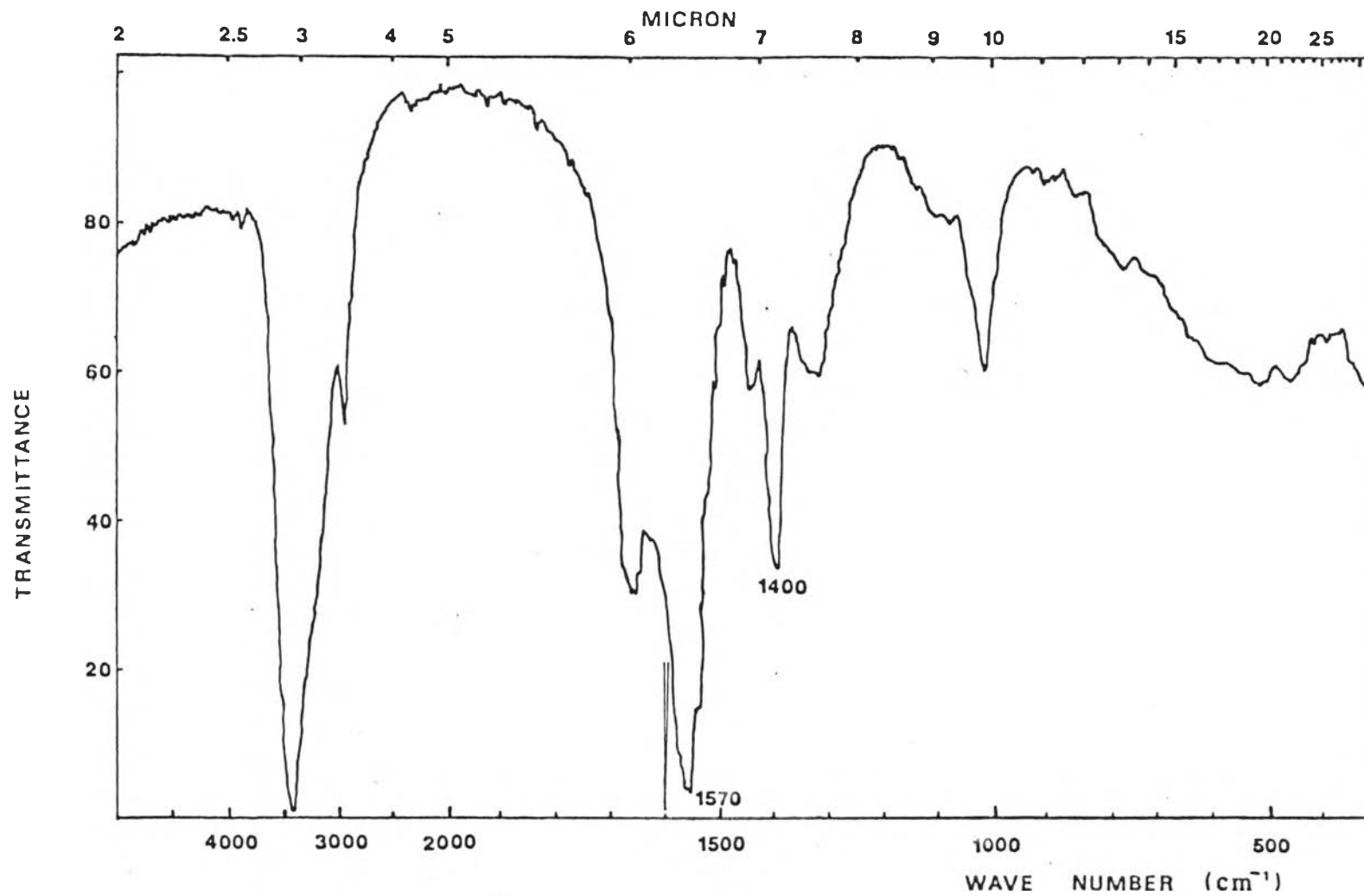


Figure 3.5 IR spectrum of saponified starch-g-PAN



the homopolymer, PAN, which occurred as a by-product during the grafting reaction. When the graft copolymer was saponified, all CN groups were hydrolyzed into the carboxylate and carboxamide groups and resulted in the disappearance of the nitrile stretching peak. The formation of two new functional groups resulted also in two new absorption bands in the IR spectrum. Indeed in Figure 3.5, the carboxylate group  $-COOK$  gave rise to two bands : a strong asymmetrical stretching band at  $1570\text{ cm}^{-1}$ , and a weak, symmetrical stretching band at  $1400\text{ cm}^{-1}$  [31]. On the other hand, the primary amide could not be detected, probably as a result of a relatively low concentration and/or due to the usually low intensity of the NH stretching band and overlapping with existing absorption bands of the starting material.

Figure 3.6 shows an increase of the nitrile absorption band as the amount of acrylonitrile to be used for the grafting reaction was increased from 5 to 20 ml.

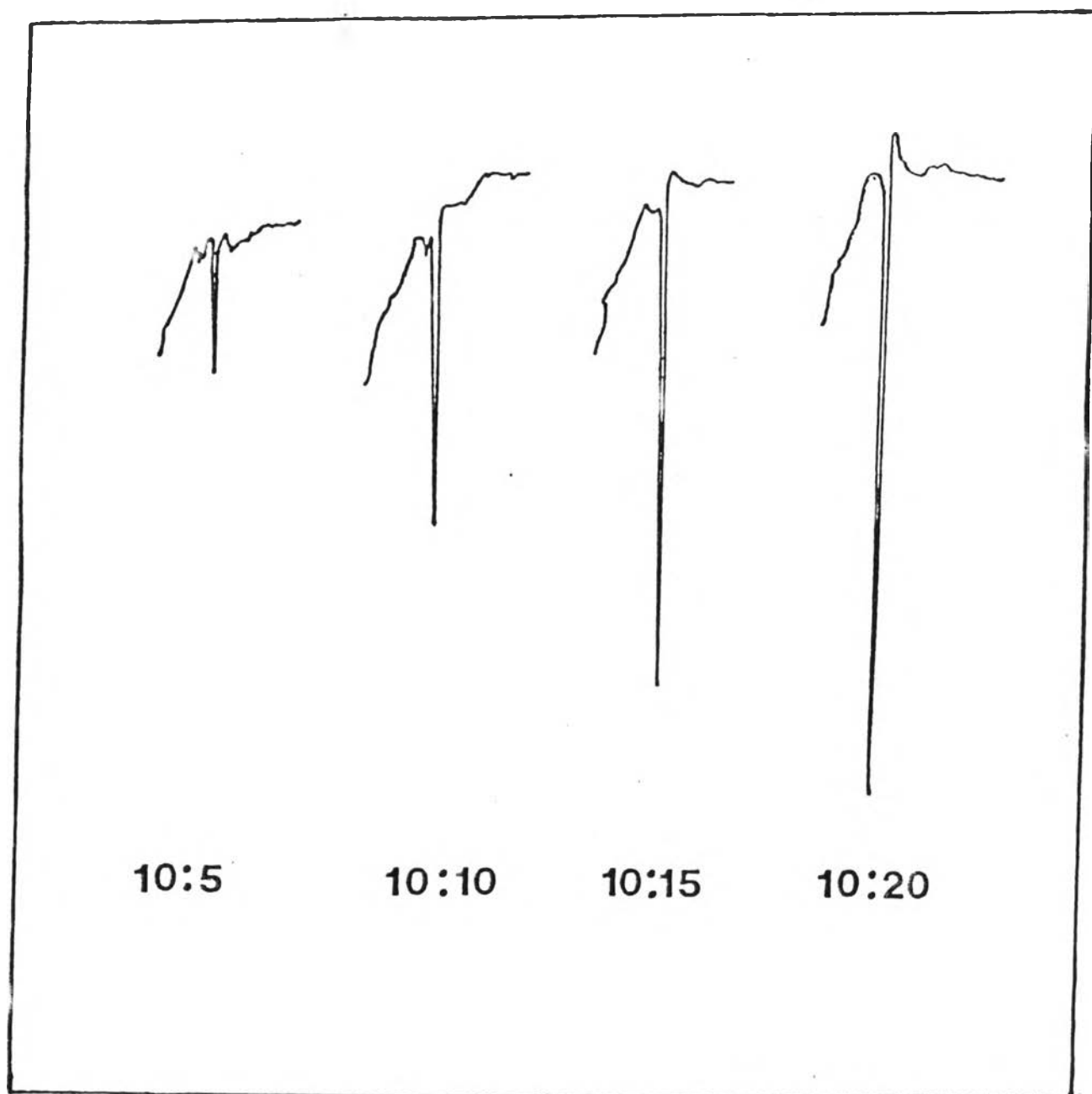


Figure 3.6 The CN peak of starch-g-PAN with different starch(g) / AN(ml) ratios

### 3.2.2 Effect of the concentration of acrylonitrile on:

#### (a) Amount of homopolymer

In order to determine the amount of the homopolymer formed during the grafting reaction, the resulting copolymer was put in DMF. PAN is soluble in this solvent while the grafted starch is not. The IR spectrum in Figure 3.4 shows the purified starch-g-PAN. The percent of homopolymer formed varied from 6.12% to 15.85% as indicated in Table 3.1. The homopolymer content increased only slightly with increasing amount of acrylonitrile.

In order to elucidate the formation of homopolymer, we carried a reaction using acrylonitrile only with the same catalyst system for 3 hrs. No polyacrylonitrile resulted from this experiment, thus indicating that  $Mn^{3+}$  did not initiate the homopolymerization. This suggests that the formation of polyacrylonitrile is a result of chain transfer reactions which increased with increasing the acrylonitrile content.

#### (b) Grafting efficiency

The highest grafting efficiency was obtained with the lowest concentration of AN. It decreases from 93.80 to 84.15% as the concentration of AN is increased from 2.5 to 30.0 ml. The trend of the grafting efficiency is illustrated in Table 3.1 and Figure 3.7.

Table 3.1 Experimental data of graft copolymerizations carried out with 10 g of cassava starch (8.72 g dry weight). Reaction conditions :  $Mn^{3+} = 1$  mmole/L;  $[Na_4P_2O_7] = 10$  mmole/L;  $H_2SO_4 = 85.8$  mmole/L; reaction temperature,  $35^\circ C$ ; reaction time, 3 hrs; gelatinization at  $65^\circ C$ .

Starch (g)/AN (ml) ratio	Homopolymer formed (%)	Grafting efficiency (%)	Percent add-on
10: 2.5	6.12	93.88	9.45
10: 5.0	8.99	91.01	26.39
10: 7.5	8.40	91.60	38.11
10:10.0	9.36	90.64	44.48
10:12.5	9.87	90.13	56.55
10:15.0	14.47	85.53	60.31
10:17.5	14.21	85.79	62.68
10:20.0	12.05	87.95	67.52
10:25.0	15.85	84.15	68.11
10:30.0	15.43	84.57	67.93

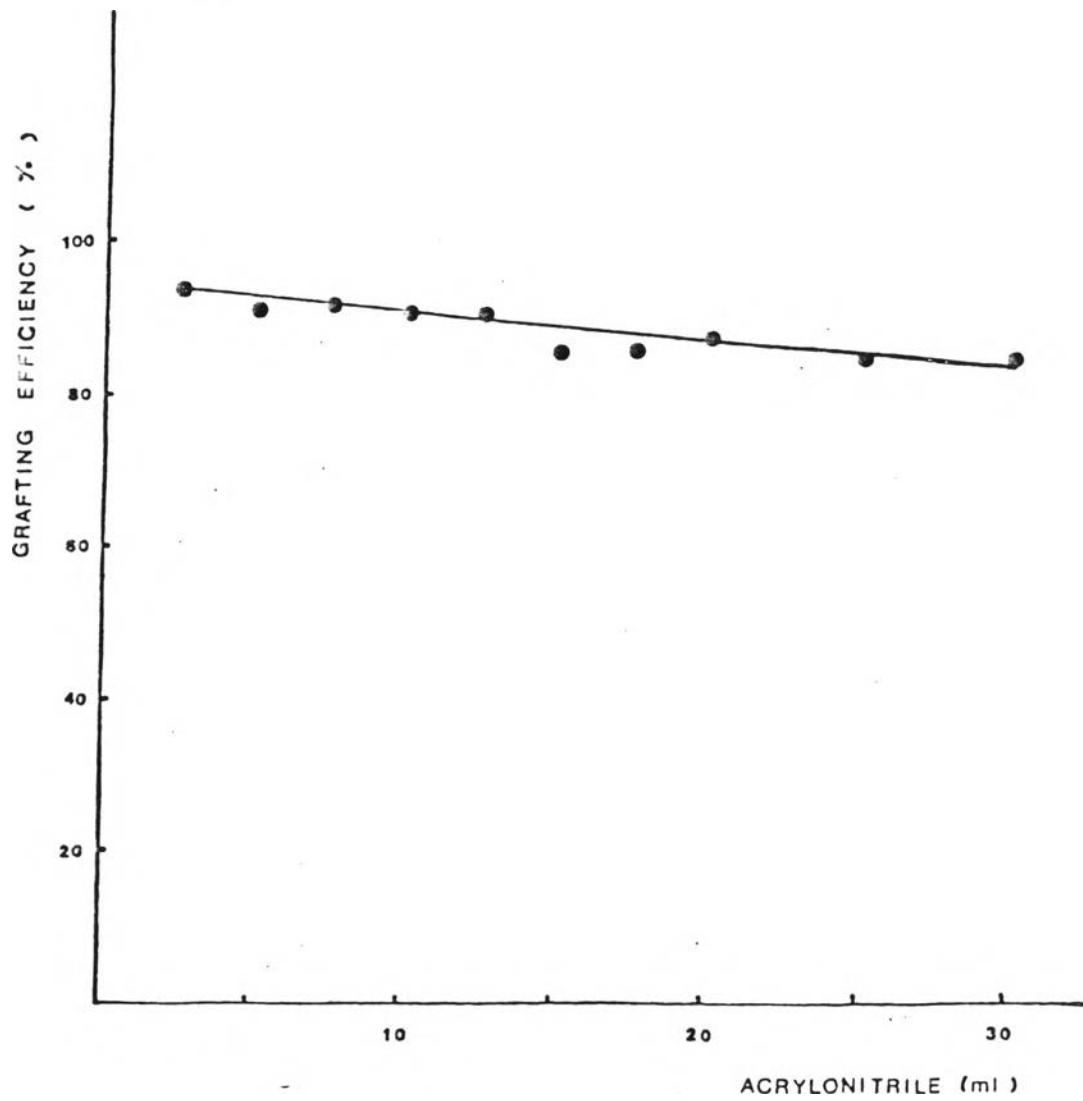


Figure 3.7 Effect of the concentration of acrylonitrile on grafting efficiency

(c) Percent add-on

The effect of the concentration of acrylonitrile on the % add-on is shown in Table 3.1 and Figure 3.8. The increase of acrylonitrile from 2.5 to 30.0 ml resulted in an increase of the % add-on from 9.45% to 67.52%, and then leveled off after 20 ml.

(d)  $\bar{M}_v$  and grafting frequency

The data of the effect of the concentration of acrylonitrile on  $\bar{M}_v$  and the grafting frequency are given in Table 3.2 and illustrated in Figure 3.9. When increasing the amount of acrylonitrile from 2.5 to 30.0 ml, the  $\bar{M}_v$  of starch-g-PAN increased from 61,500 to 568,900, while the number of AGU/graft reduced from 6,689 to 1,658. A plateau of  $\bar{M}_v$  and grafting frequency occurred after more than 17.5 ml of acrylonitrile was used for the reaction. A similar trend of the % add-on with the same catalyst system was already observed.

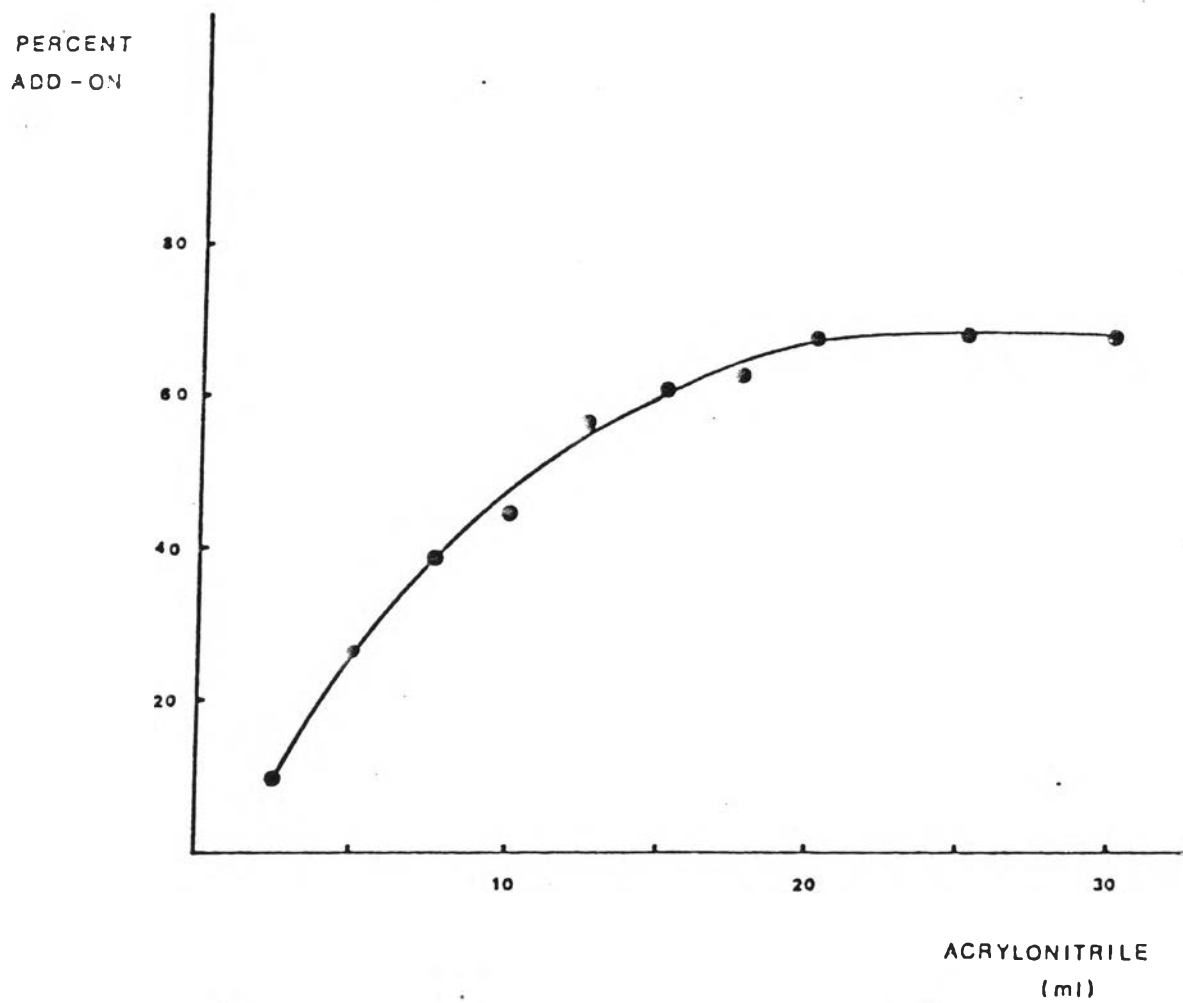


Figure 3.8 Effect of the concentration of acrylonitrile on % add-on

Table 3.2 Viscosity average molecular weight ( $\bar{M}_v$ ) and grafting frequency data of starch-g-PAN.  
(same reaction condition as in Table 3.1)

Starch (g)/AN (ml) ratio	Molecular weight ( $\bar{M}_v$ )	Grafting frequency (AGU/chain)
10: 2.5	61,500	3,634
10: 5.0	388,500	6,689
10: 7.5	427,200	4,282
10:10.0	465,000	3,582
10:12.5	500,900	2,375
10:15.0	543,800	2,209
10:17.5	579,200	2,128
10:20.0	566,100	1,681
10:25.0	564,200	1,630
10:30.0	568,900	1,658



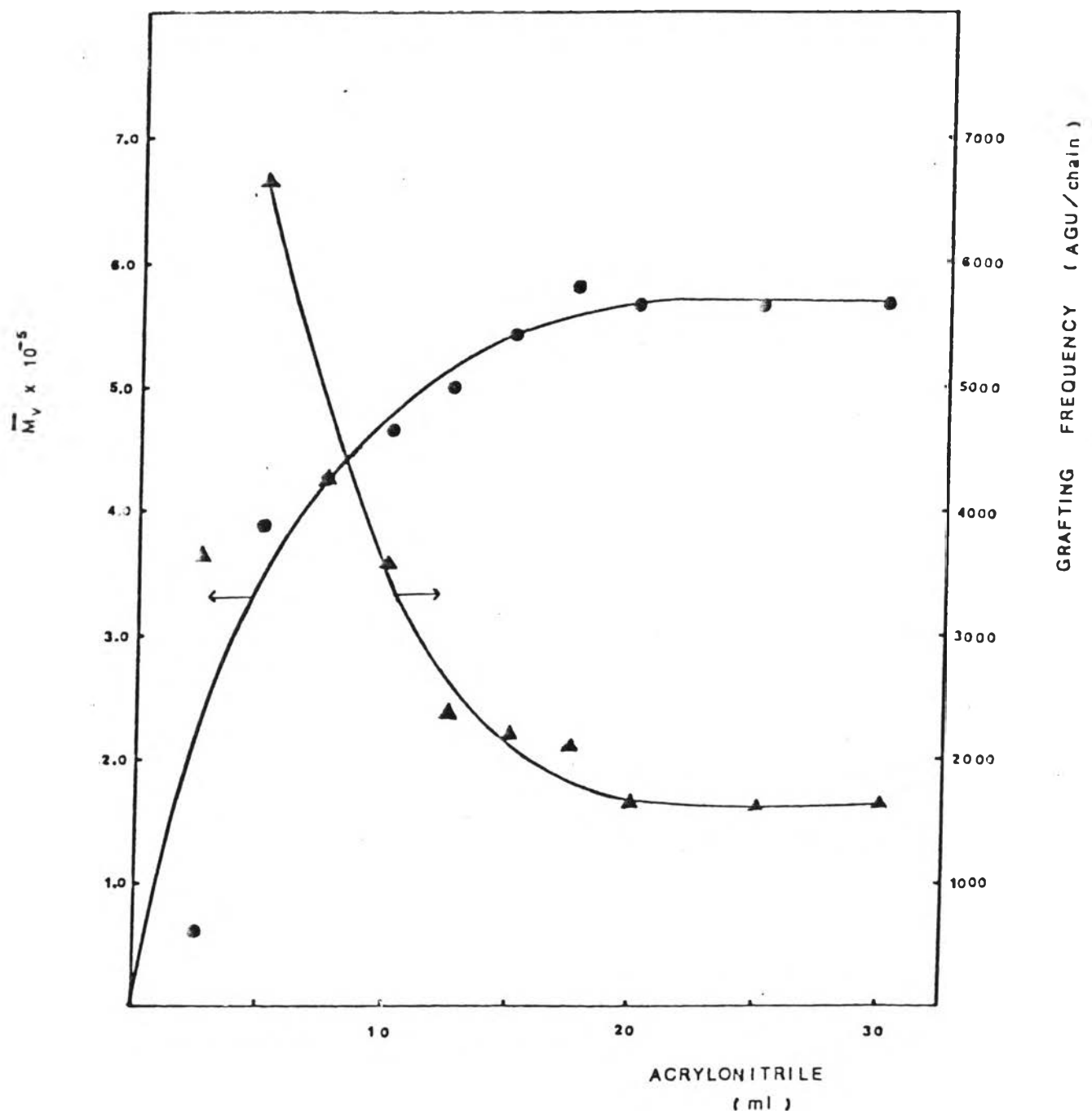


Figure 3.9 Effect of the contraction of acrylonitrile on  $\bar{M}_v$  and grafting efficiency. ● denotes  $\bar{M}_v$  while ▲ represents grafting frequency

### 3.2.3 Saponification of starch-g-PAN

Starch-g-PAN was saponified in various KOH concentration at 0.85%, 4.25%, and 8.5% w/v. At 8.5% KOH a deep-red color develops during the hydrolysis, due to intermediate formation of naphthyridine structures from adjacent nitrile groups [23]. The intermediate rings are subsequently hydrolyzed causing a change in color from red to light yellow. At lower concentration (0.85% and 4.25%), however, the deep-red color did not develop. The color was only orange and it remained so for the rest of the reaction. This may be due to a lower concentration of the OH groups hydrolyzing only a small amount of the nitrile groups. This is evidenced by IR analysis of the saponified starch-g-PAN at 0.85% KOH when compared with 8.5% KOH as shown in Figures 3.10 and 3.11. At a concentration of 0.85% KOH the CN absorption band still remained, but at 8.5% KOH the same peak disappeared indicating complete saponification of the CN groups. On the basis of these results all saponification reactions were carried out at a 8.5% KOH concentration.

The effect of the saponified starch-g-PAN at different KOH concentration on the water absorption in deionized water is shown in Table 3.3. The product of the 10:20.0 ratio was used for this study. The results indicate that at higher KOH concentration, saponification of the nitrile group was greater and completed, thus yielding a higher concentration of amide and salt groups, and therefore

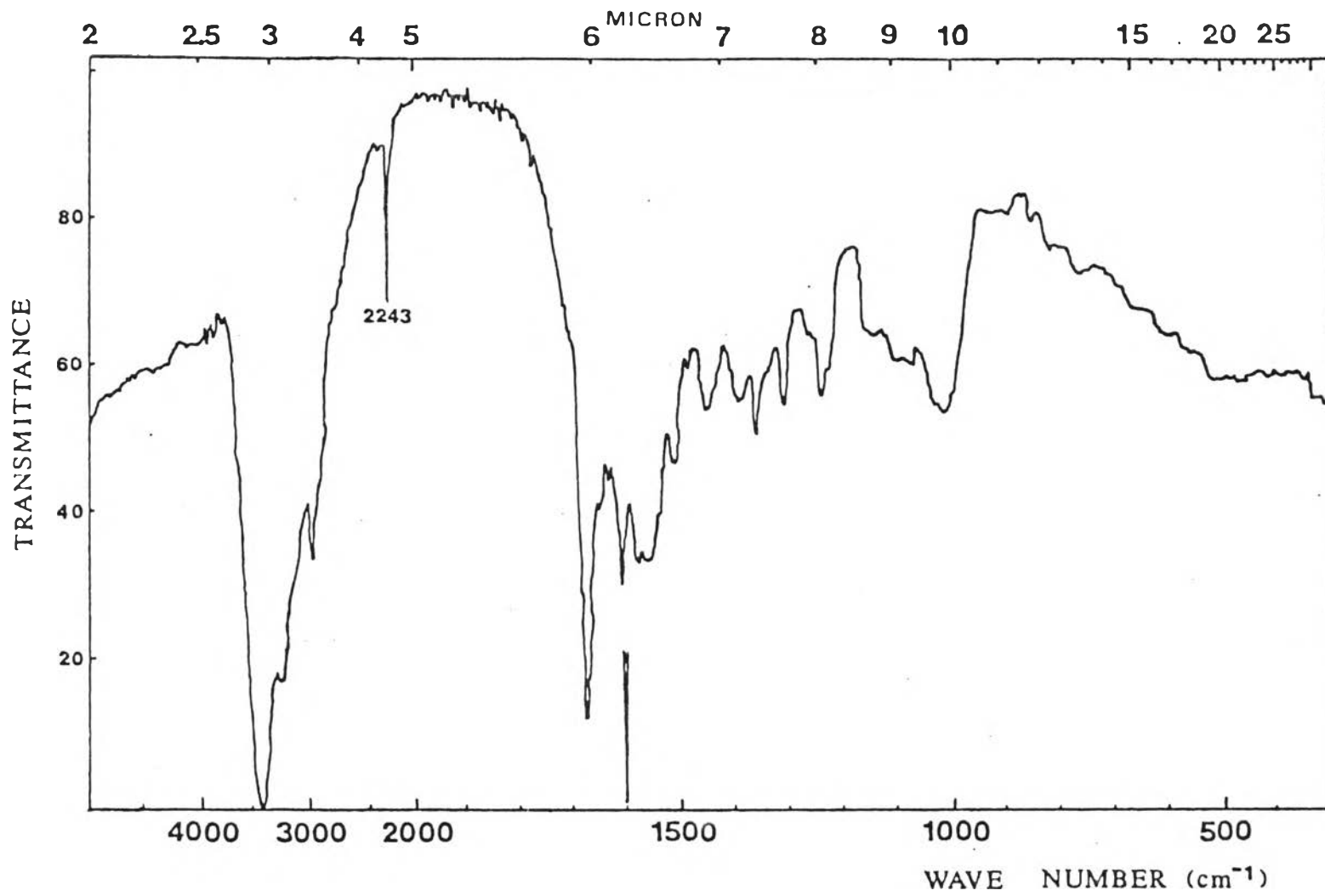


Figure 3.10 IR spectrum of starch-g-PAN saponified with 0.85 % KOH

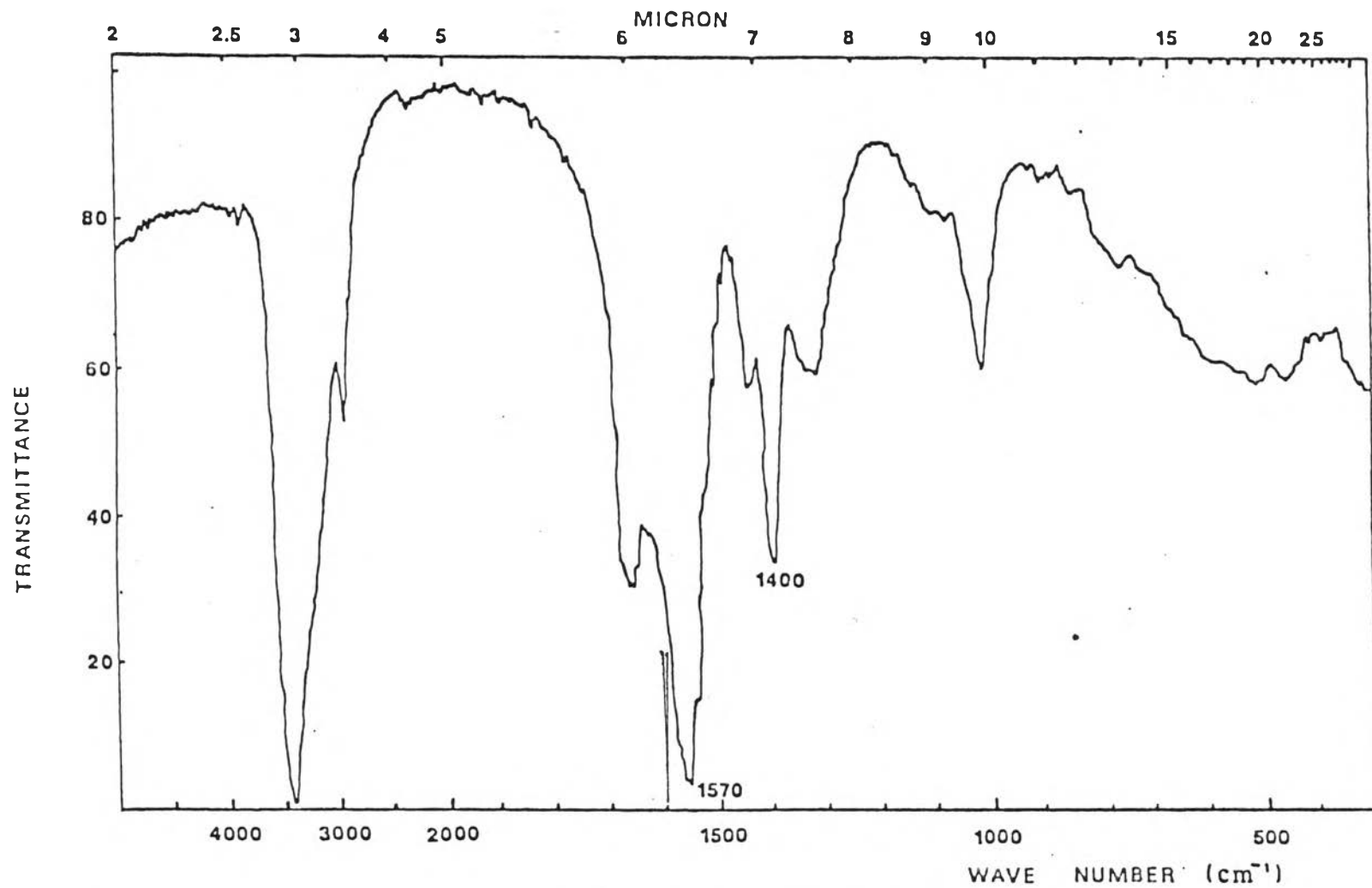


Figure 3.11 IR spectrum of starch-g-PAN saponified with 8.5 % KOH

inducing a higher osmotic pressure, which subsequently resulted in a higher water intake by the polymer gel. The reaction which takes place during saponification, and which is paramount to the water absorption properties of HWAP, is the following reaction [32]:



Table 3.3 Different KOH concentrations used during saponification and their effect on water absorption.

Concentration of KOH (% w/v)	Water absorption in deionized water (g/g)
0.85	14.1
4.25	125.4
8.50	220.7

### 3.2.4 Water absorption in deionized water

A further investigation led us to consider the effect on water absorption by increasing the concentration of acrylonitrile while keeping the concentration of starch constant during the grafting reaction. The experimental data which are given in Table 3.4 and plotted in Figure 3.12, show the concentration of acrylonitrile as a function of water absorption.

Table 3.4 Water absorption as a function of acrylonitrile concentration (gelatinization temperature 65°C).

Starch(g)/AN(ml) ratio	Water absorption in deionized water (g/g)
10: 2.5	39.8
10: 5.0	81.7
10: 7.5	107.3
10: 10.0	162.1
10: 12.5	185.7
10: 15.0	206.6
10: 17.5	220.3
10: 20.0	220.7
10: 25.0	221.4
10: 30.0	221.5

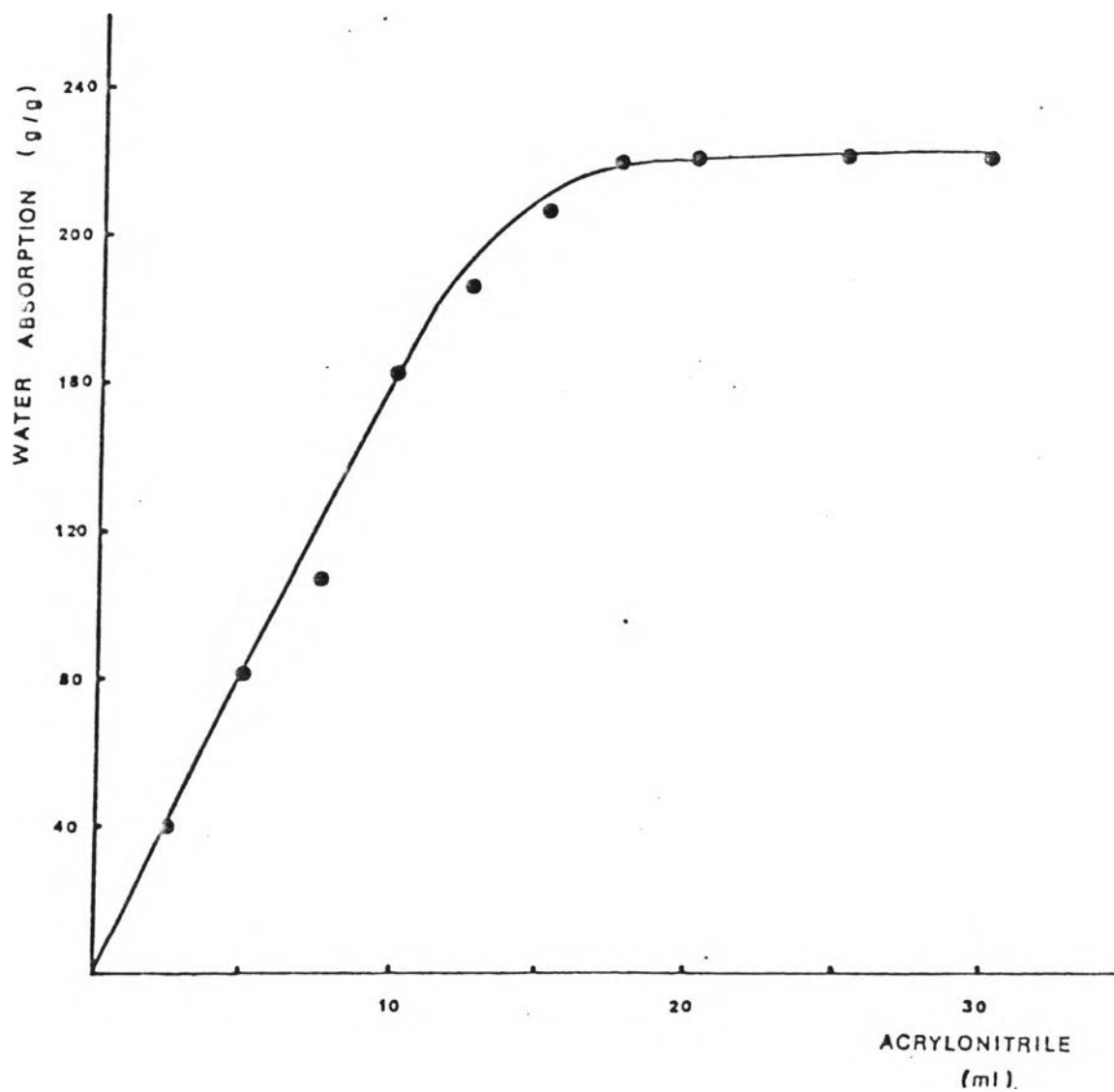


Figure 3.12 Water absorption of saponified starch-g-PAN as a function of acrylonitrile

A plateau of the water absorption occurred at a concentration of 17.5 ml acrylonitrile. This same trend was already observed in Figures 3.8 and 3.9 correlating the % add-on and  $\overline{M}_v$  with the concentration of AN. It also suggests that the water absorption is a function of the % add-on and  $\overline{M}_v$ . Figure 3.13 shows that the correlation between the % add-on and water absorption is a linear relationship.

The above findings correlate well with the mechanistic model of the enhanced water sorbence of acrylate-grafted polysaccharides [33] that is essentially the same as that described by Grignon and Scallman for the swelling of cellulose gels [34]. Here 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. In our case, the concentration of mobile  $K^+$  ions in the gel is higher than in deionized water. The fundamental feature within the gel, bringing about the unequal distribution, is the presence of the potassium carboxylate and carboxamide groups attached to the macromolecular network. As the acidic 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 the acidic groups attached to the macromolecular network but gives free passage of water and simple ions. The gel swells as a result of the entry of water in an attempt to reduce the osmotic pressure differential resulting from the



difference in ion concentrations. Swelling continues until the osmotic pressure differential is equal to the resistance to further expansion, that is, when the ion concentration between inside and outside the gel has reached equilibrium.

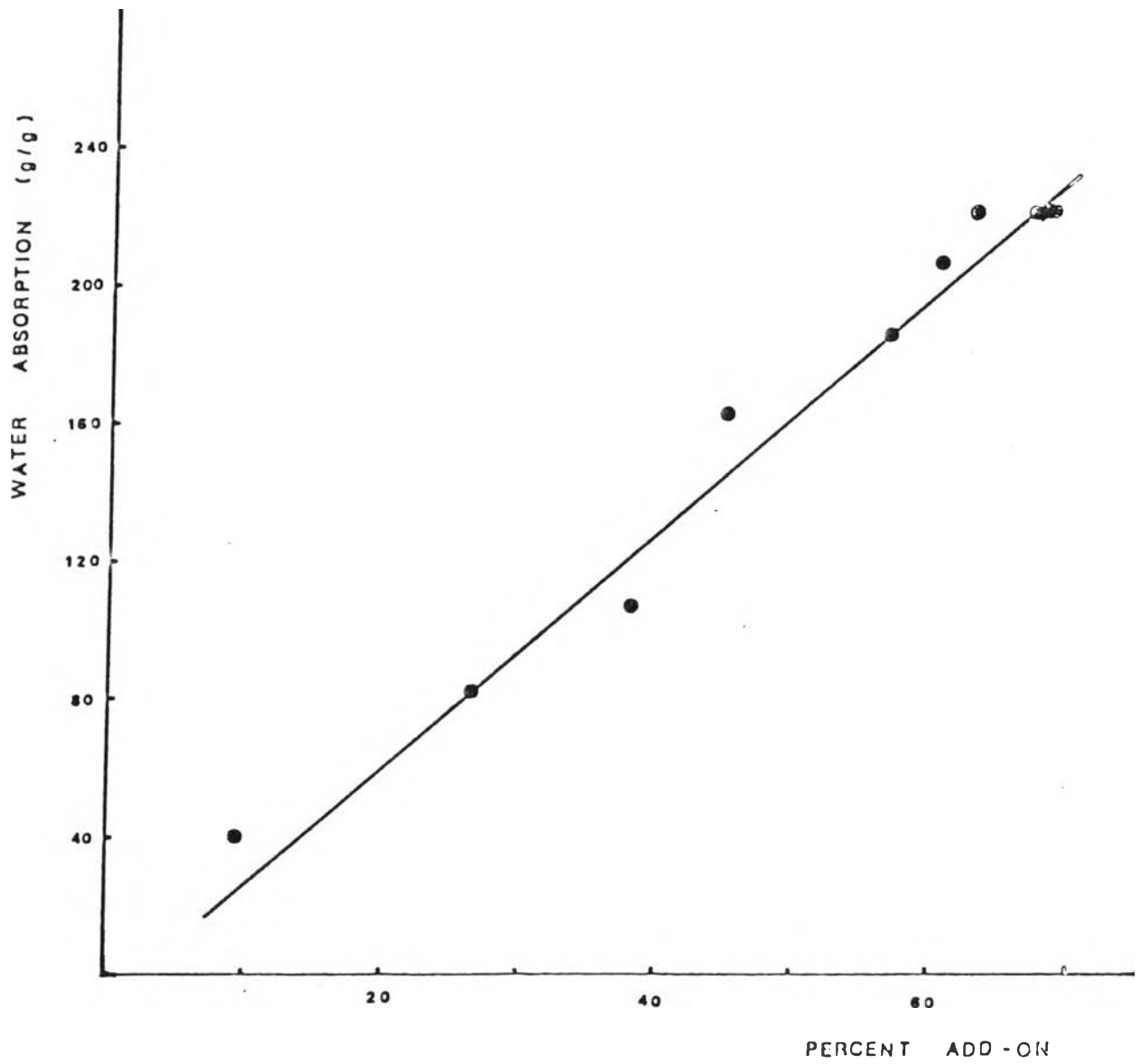


Figure 3.13 Water absorption as a function of % add-on

### 3.2.5 Water absorption in aqueous salt solutions

So far water absorption was determined using deionized water in order to obtain maximum absorption since in this case we had maximum ion concentration difference between inside and outside the gel. Now it is of interest to determine the effect of different salt solutions at different concentrations. We have chosen NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> salts which are commonly found in soils, and for each salt, solutions of 0.5, 1.0, and 2.0% w/v were prepared. The water absorption data are given in Tables 3.5- 3.7 and their plots at different salt concentrations in Figures 3.14-3.16 illustrate the ion effect.

The water absorption data using NaCl are given in Table 3.5 and plotted in Figure 3.14. All the curves indicate that water absorption decreases dramatically with increasing salt concentration, and when compared with deionized water. At the (10:12.5) ratio, all three curves begin to reach a plateau indicating that the osmotic pressure inside and outside the gel had reached equilibrium.

As observed in the case of NaCl, the water absorption decreases as CaCl<sub>2</sub> concentration increase. However, here the curves at 1% and 2% CaCl<sub>2</sub> concentration are almost identical, with the 1% having a slightly higher water absorption only. This suggests that the osmotic pressure equilibrium was reached earlier in the presence of the divalent ion. As a consequence, the water absorption

with  $\text{CaCl}_2$  is much less than with  $\text{NaCl}$ , here the optimum absorbency is less than 24 g/g while for  $\text{NaCl}$  we obtained about 70 g/g.

In the case of  $\text{MgCl}_2$ , a plateau was reached even earlier with a maximum water absorption of only 20 g/g with the 0.5% solution. The 1% and 2% concentrations curves are identical.

Table 3.5 Effect of different sodium chloride solutions  
on water absorption

Starch(g)/AN(ml) ratio	Water absorption in 0.5% NaCl (g/g)	Water absorption in 1% NaCl (g/g)	Water absorption in 2% NaCl (g/g)
10: 2.5	17.9	10.3	16.1
10: 5.0	36.5	18.7	18.5
10: 7.5	48.9	32.4	20.1
10:10.0	59.8	37.3	31.5
10:12.5	67.0	50.7	33.7
10:15.0	69.3	53.7	34.9
10:17.5	68.6	50.1	36.8
10:20.0	69.3	51.4	32.2
10:25.0	70.1	50.1	33.4
10:30.0	69.0	49.6	32.0

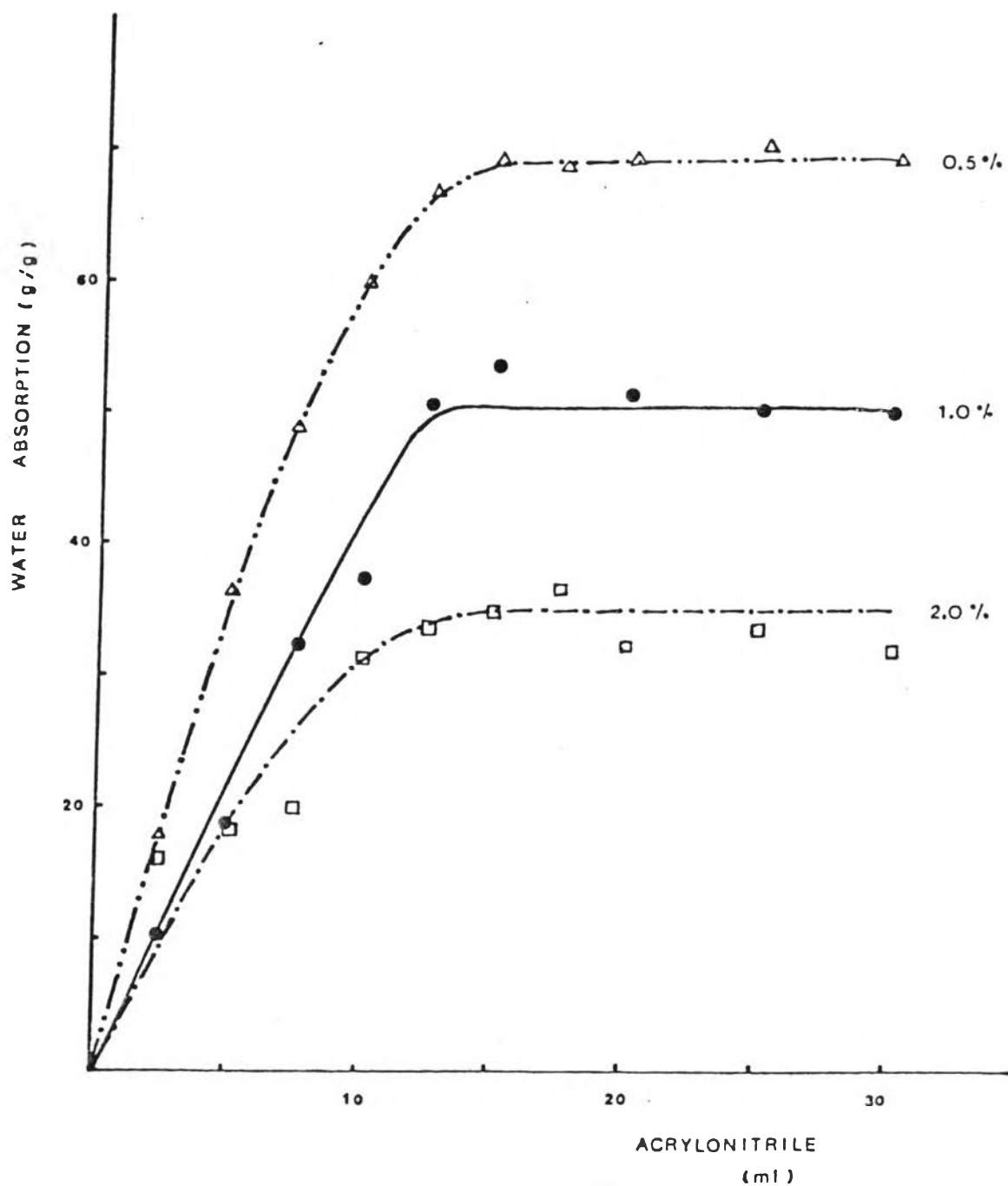


Figure 3.14 Water absorption in NaCl solutions of 0.5 %, 1.0 %, and 2.0 % w/v concentrations

Table 3.6 Effect of different calcium chloride solutions on water absorption

Starch(g)/AN(ml) ratio	Water absorption in 0.5% CaCl <sub>2</sub> (g/g)	Water absorption in 1% CaCl <sub>2</sub> (g/g)	Water absorption in 2% CaCl <sub>2</sub> (g/g)
10: 2.5	8.6	4.3	4.2
10: 5.0	15.1	8.6	8.3
10: 7.5	17.7	11.9	11.3
10:10.0	19.3	13.2	13.1
10:12.5	23.3	14.5	14.3
10:15.0	23.3	14.3	13.9
10:17.5	25.4	15.3	14.9
10:20.0	23.1	15.9	15.2
10:25.0	22.3	15.1	14.9
10:30.0	23.8	15.1	14.7

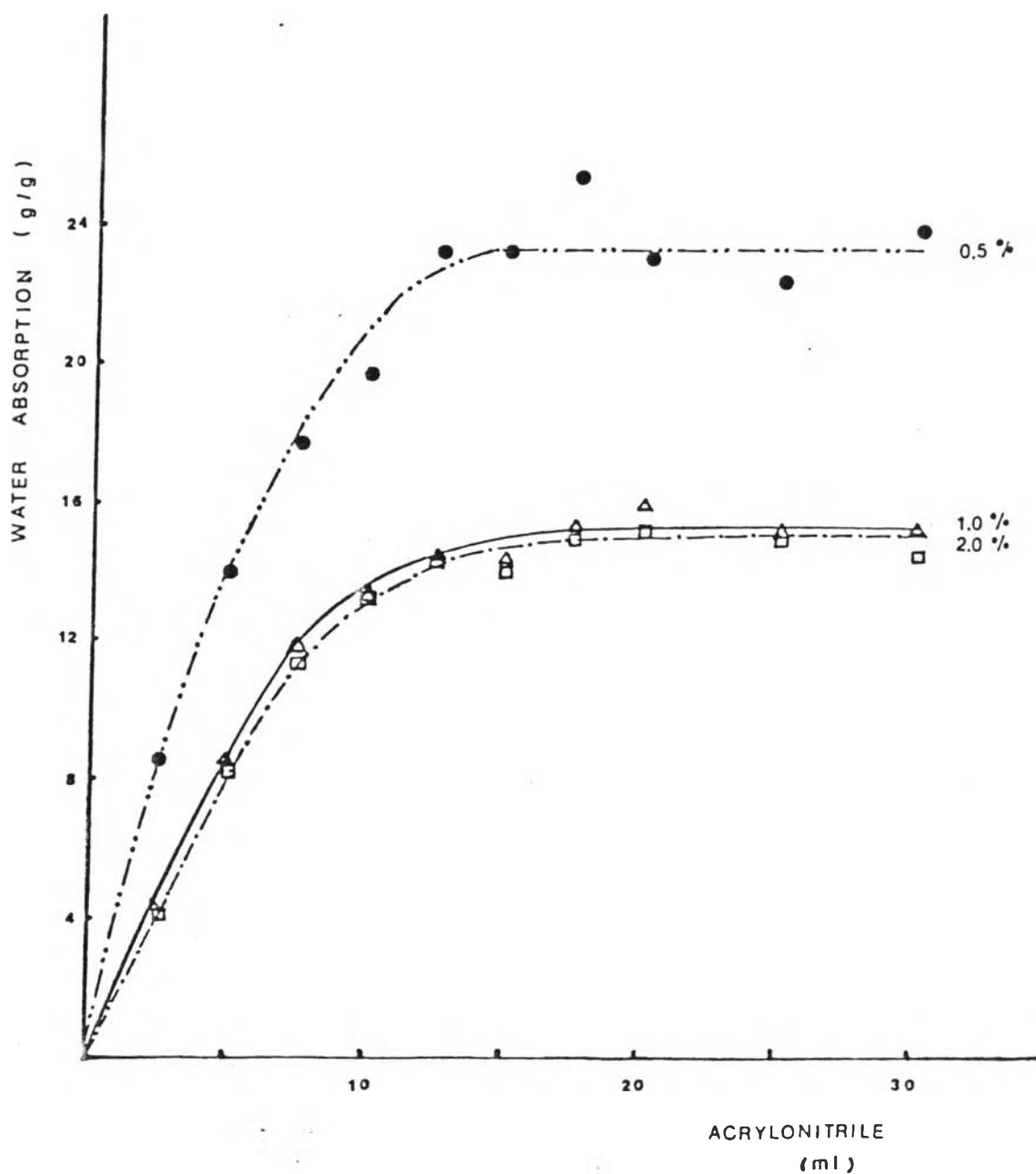


Figure 3.15 Water absorption in  $\text{CaCl}_2$  solutions of 0.5 %, 1.0 %, and 2.0 % w/v concentrations



Table 3.7 Effect of different magnesium chloride solutions on water absorption

Starch(g)/AN(ml) ratio	Water absorption in 0.5% MgCl <sub>2</sub> (g/g)	Water absorption in 1% MgCl <sub>2</sub> (g/g)	Water absorption in 2% MgCl <sub>2</sub> (g/g)
10: 2.5	9.0	14.5	13.2
10: 5.0	10.6	13.2	13.3
10: 7.5	17.7	14.4	13.6
10:10.0	18.0	13.7	14.4
10:12.5	18.6	14.5	14.3
10:15.0	19.3	14.5	14.3
10:17.5	19.3	14.8	14.2
10:20.0	19.4	14.4	14.5
10:25.0	18.8	14.9	15.0
10:30.0	19.9	14.4	14.7

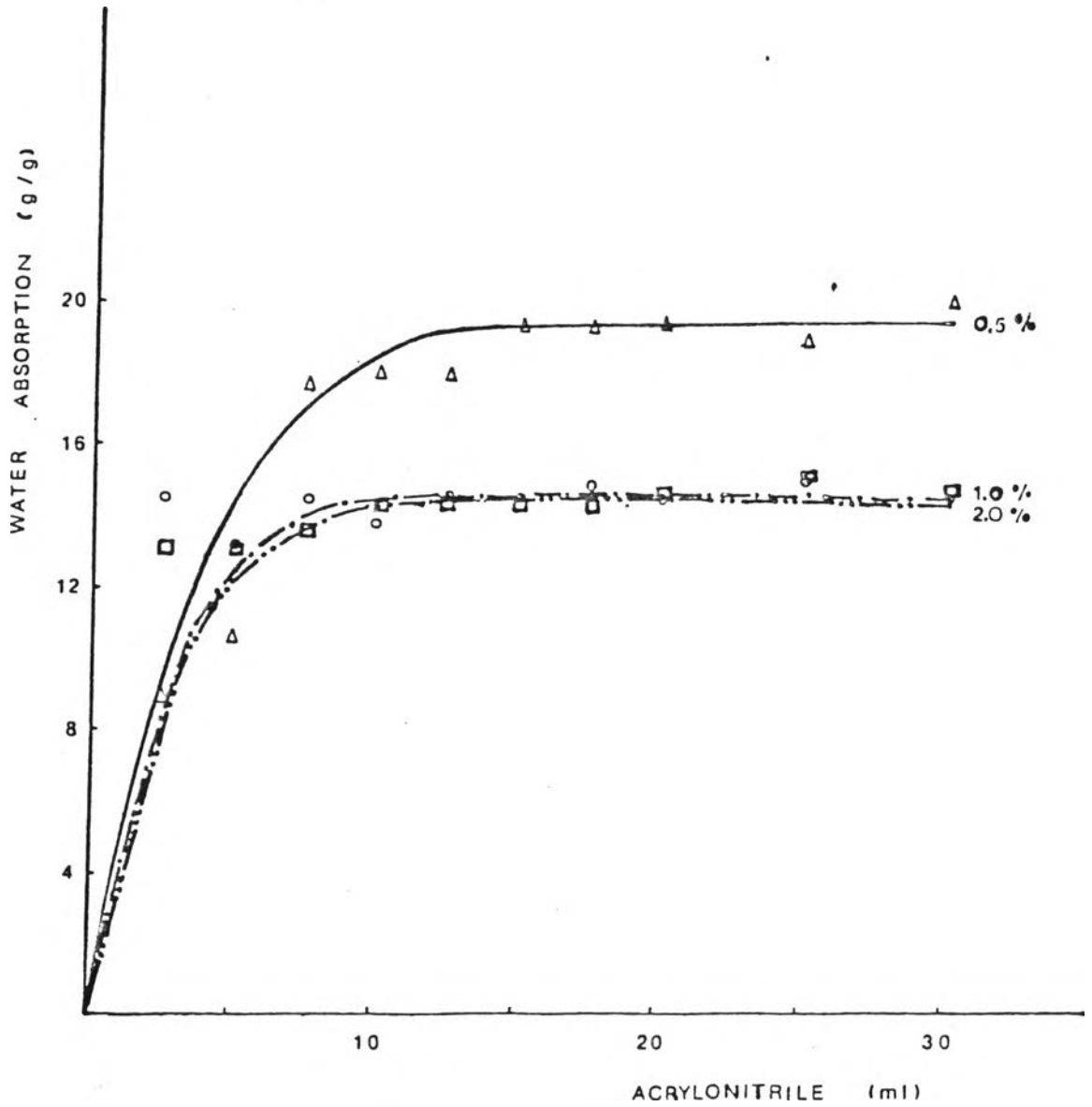


Figure 3.16 Water absorption in  $\text{MgCl}_2$  solutions of 0.5 %, 1.0 %, and 2.0 % w/v concentrations

The water absorption of the starch based superabsorbent in deionized water as compared to the water absorption in 0.5% w/v of NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub> is shown in Figure 3.17. As a function of the amount of acrylonitrile, the absorption in deionized water and salt solutions exhibit the same pattern. The figure indicates an increase at lower concentration of acrylonitrile and then levels off at around 15.0 ml of AN. The salt effect is clearly evidenced as a result of the osmotic pressure differential between the internal solution in the gel and external solution, due to the different ion concentrations [34]. The water intake by the gel reduced the osmotic pressure until an ion concentration equilibrium was reached.

At same salt concentration, the water absorption decreased in the following order: NaCl > CaCl<sub>2</sub> > MgCl<sub>2</sub>. The sodium ion is monovalent while calcium and magnesium ions are divalent. This suggests that an ion equilibrium between inside and outside the gel was reached much more slowly when a monovalent ion was used instead of a divalent ion, as a result of a higher water intake. Such an equilibrium was reached much faster with divalent ions.

Regarding the difference in water absorption between CaCl<sub>2</sub> and MgCl<sub>2</sub>, the former absorbs more. This difference may be due to the respective electronic configuration of Ca<sup>2+</sup> and Mg<sup>2+</sup>, as well as in their difference in ionizing efficiency.

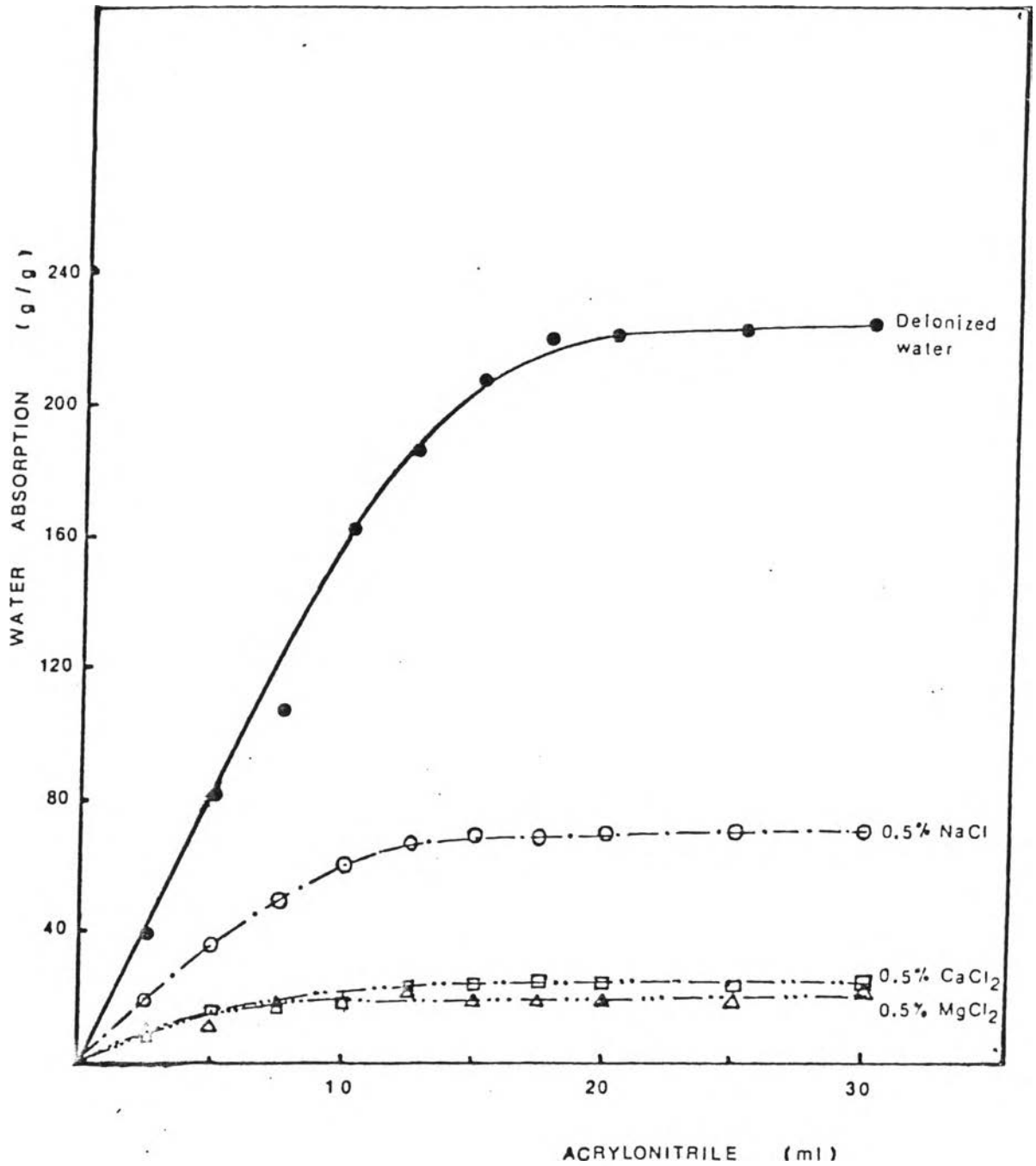


Figure 3.17 A comparison of water absorption between deionized water and 0.5 % w/v salt solutions of NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>

### 3.3 Grafting of acrylonitrile onto starch gelatinized at 80 °C

#### 3.3.1 Effect of the concentration of acrylonitrile on:

The grafting reaction of acrylonitrile onto starch gelatinized at 80 °C led to the experimental data in Table 3.8.

##### (a) Amount of homopolymer

The amount of homopolymer formed varied from 7.20 to 12.99% as shown in Table 3.8. Comparing Tables 3.1 and 3.8 indicates that the homopolymer formation is reduced at a higher gelatinization temperature when increasing the AN concentration. This is in agreement with other investigations [20-23] where the grafting efficiency is improved at a higher gelatinization temperature (up to a limited temperature) as the polymer chain of starch becomes more accessible to grafting, thus reducing the formation of PAN.

##### (b) Grafting efficiency

The grafting efficiency is also the highest at the lowest concentration of AN. The trend of the grafting efficiency is illustrated in Table 3.8 and Figure 3.18. The grafting efficiency became higher at the higher

gelatinization temperature when comparing the data in Table 3.1 and 3.8. This does correlate with the decrease in homopolymer observed.

(c) Percent add-on

The effect of the concentration of acrylonitrile on the % add-on is illustrated in Figure 3.19. The increase of acrylonitrile made the % add-on increase from 30.49% to 67.03% without reaching a plateau as observed with the starch gelatinized at 65°C.

Table 3.8 Grafting of acrylonitrile onto starch gelatinized at 80 °C. Reaction conditions :  $Mn^{3+} = 1$  mmole/L;  $[Na_4P_2O_7] = 10$  mmole/L;  $H_2SO_4 = 85.8$  mmole/L; reaction temperature, 35 °C; reaction time, 3 hrs; gelatinization at 80 °C.

Starch(g)/ AN(ml) ratio	Homopolymer formed (%)	Grafting efficiency (%)	Percent add-on
10: 5.0	7.20	92.80	30.49
10:10.0	9.61	90.39	49.20
10:15.0	12.79	87.21	53.10
10:20.0	12.83	87.17	57.87
10:25.0	12.99	87.01	63.04
10:30.0	11.63	88.37	67.03

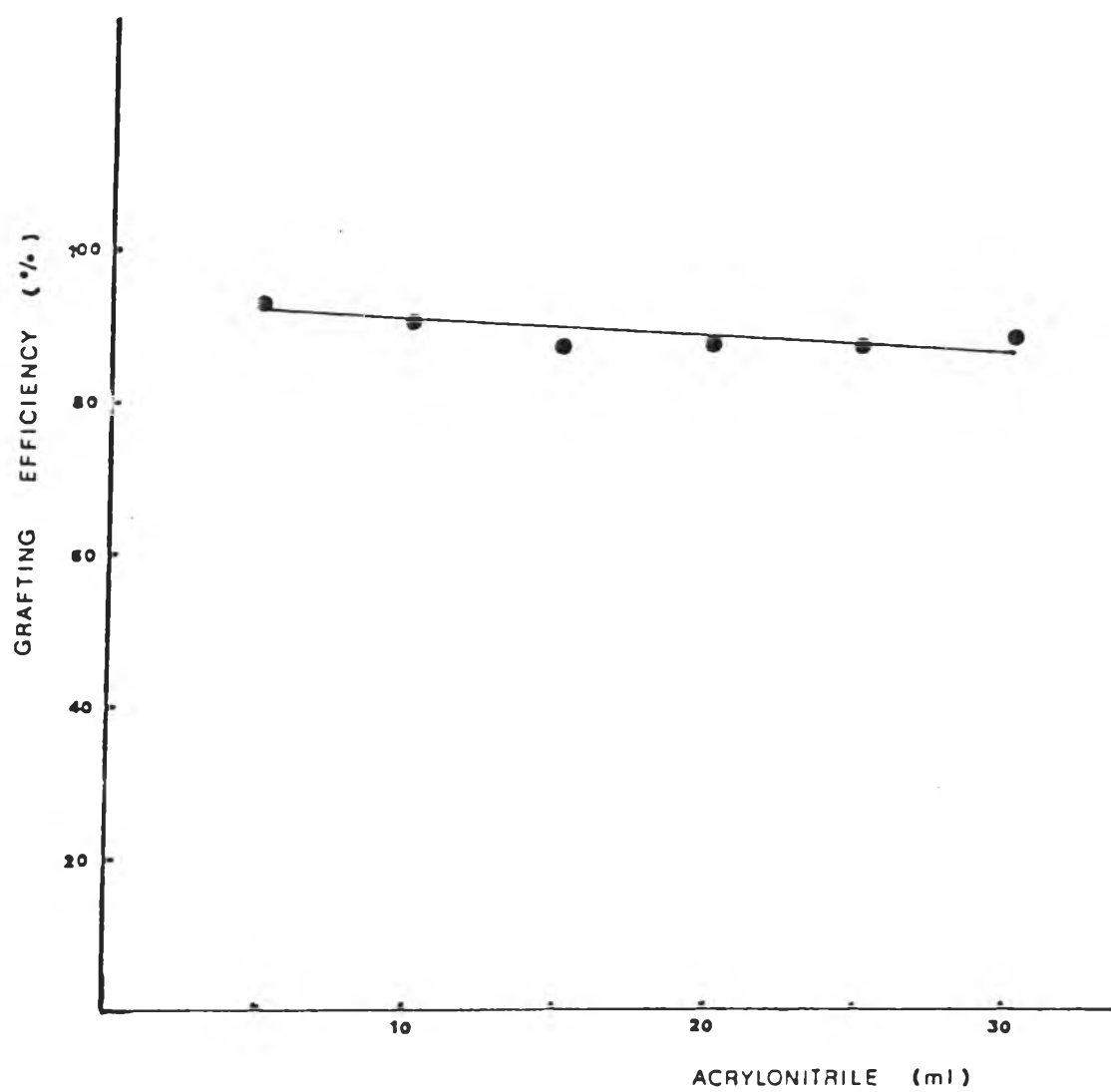


Figure 3.18 Effect of the concentration of acrylonitrile on grafting efficiency



(d)  $\bar{M}_v$  and grafting frequency

The  $\bar{M}_v$  and grafting frequency are given in Table 3.9 and plotted in Figure 3.20.  $\bar{M}_v$  increased from 382,600 to 604,700. The grafting frequency, on the other hand, decreased from 5,383 to 1,835. Comparing the data of the two different gelatinization temperatures indicates that at a higher temperature the frequency was lower for the ratios 10:5.0 and 10:10.0, but then become higher with the other ratios. This suggests that more initiator was available at a low AN concentration resulting in a higher grafting initiation frequency; while at higher AN concentration less initiator was available.

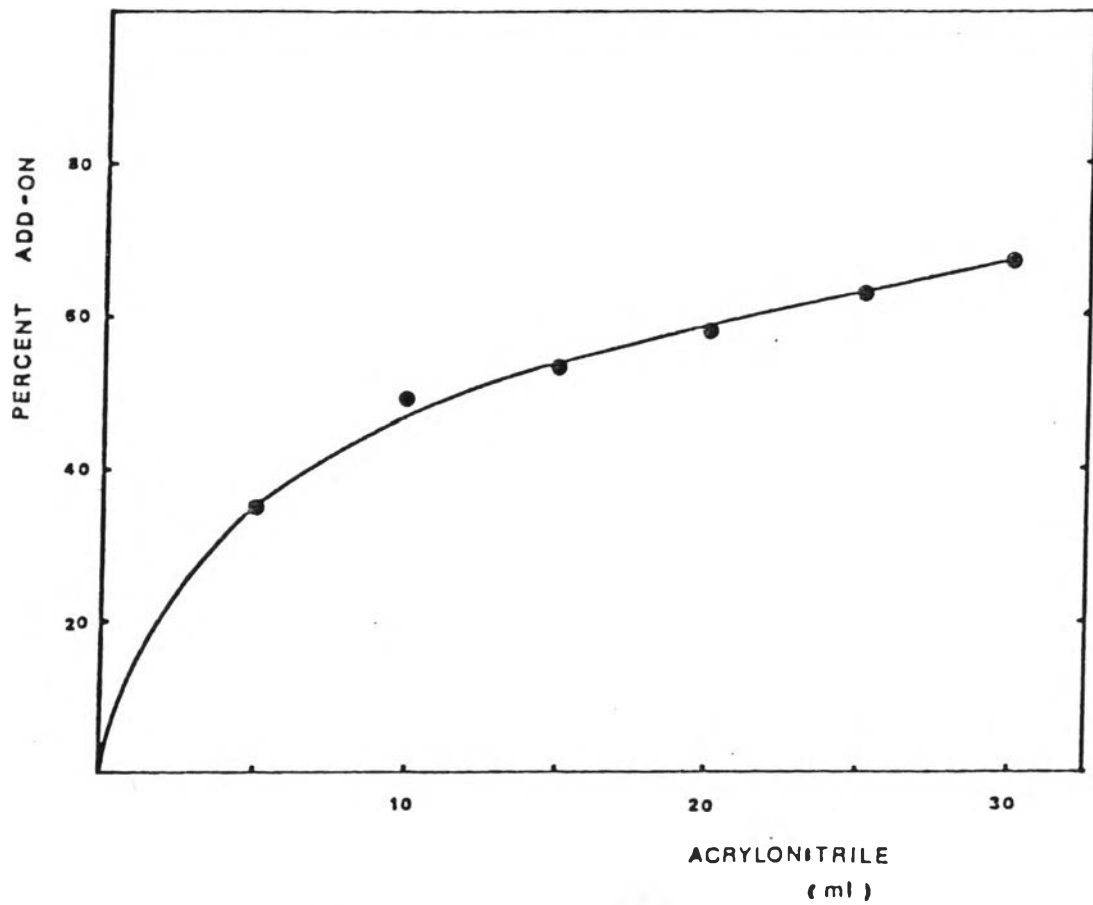


Figure 3.19 Effect of the concentration of acrylonitrile on % add-on (gelatinization at 80°C).

Table 3.9 Viscosity average molecular weight ( $\overline{M}_v$ ) and grafting frequency data of starch-g-PAN.  
(same reaction condition as in Table 3.8)

Starch(g)/AN(ml) ratio	Molecular weight ( $\overline{M}_v$ )	Grafting frequency (AGU/chain)
10: 5.0	382,600	5,383
10: 10.0	501,700	3,197
10: 15.0	550,300	3,000
10: 20.0	600,900	2,700
10: 25.0	603,700	2,184
10: 30.0	604,700	1,835

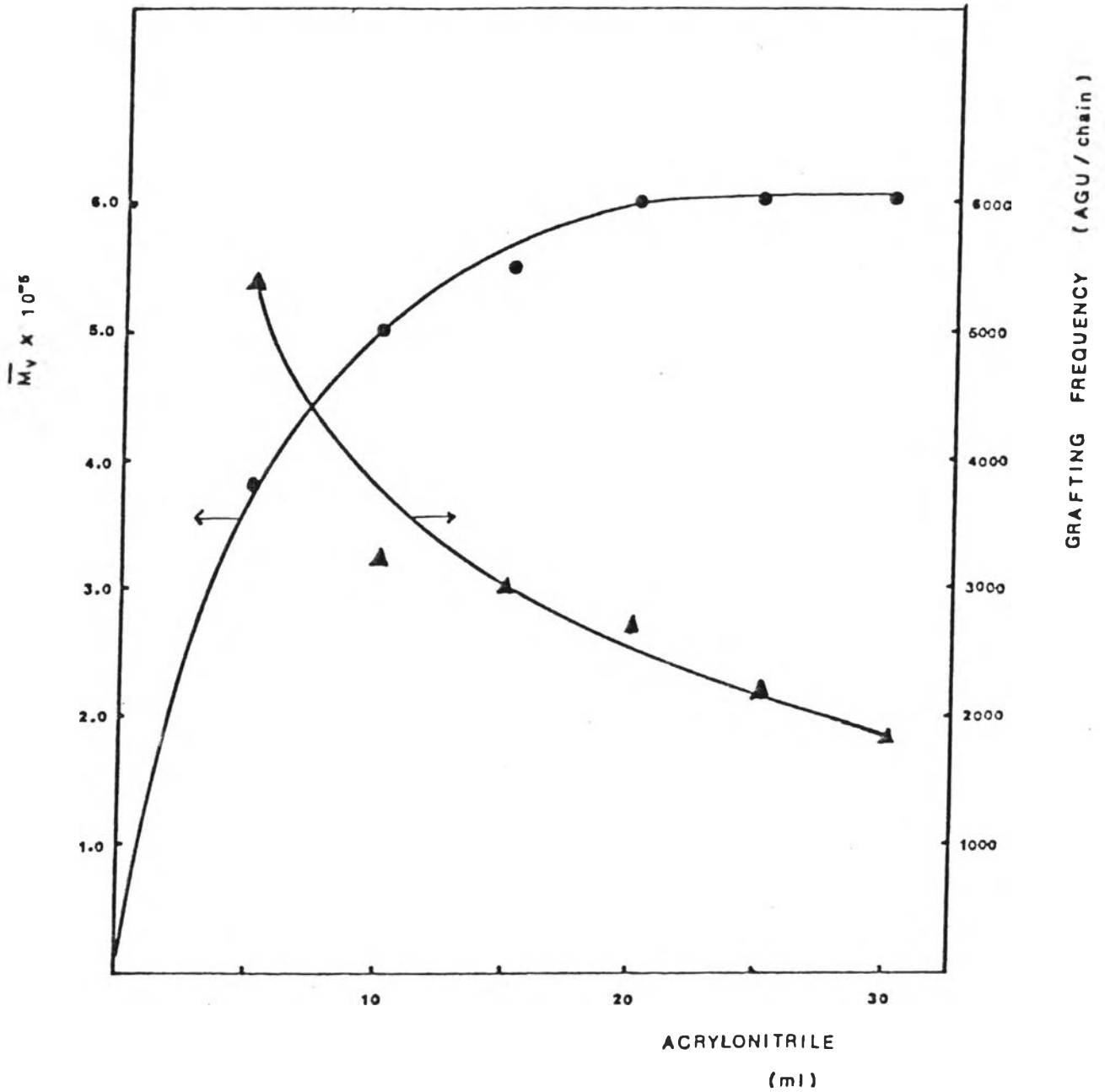


Figure 3.20 Effect of the concentration of acrylonitrile on  $\bar{M}_v$  and grafting frequency (gelatinization at 80°C). ● denotes  $\bar{M}_v$  while ▲ represents grafting frequency.

### 3.3.2 Water absorption in deionized water

The absorption in deionized water of the saponified product of 80°C gelatinized starch-g-PAN are given in Table 3.10 and illustrated in Figure 3.21. By increasing the amount of acrylonitrile from 5.0 to 30.0 ml, the water absorption increased from 118.5 to 344.5 g/g. The leveling off of the water absorption occurred at the ratio 10:20.0. Figure 3.22 shows the correlation between the % add-on and water absorption and indicates again a linear relationship for this type of graft copolymerization.

Table 3.10 Water absorption as a function of the concentration of acrylonitrile.

Starch(g)/AN(ml) ratio	Water absorption in deionized water (g/g)
10: 5.0	118.5
10:10.0	220.5
10:15.0	285.3
10:20.0	327.5
10:25.0	338.2
10:30.0	344.5

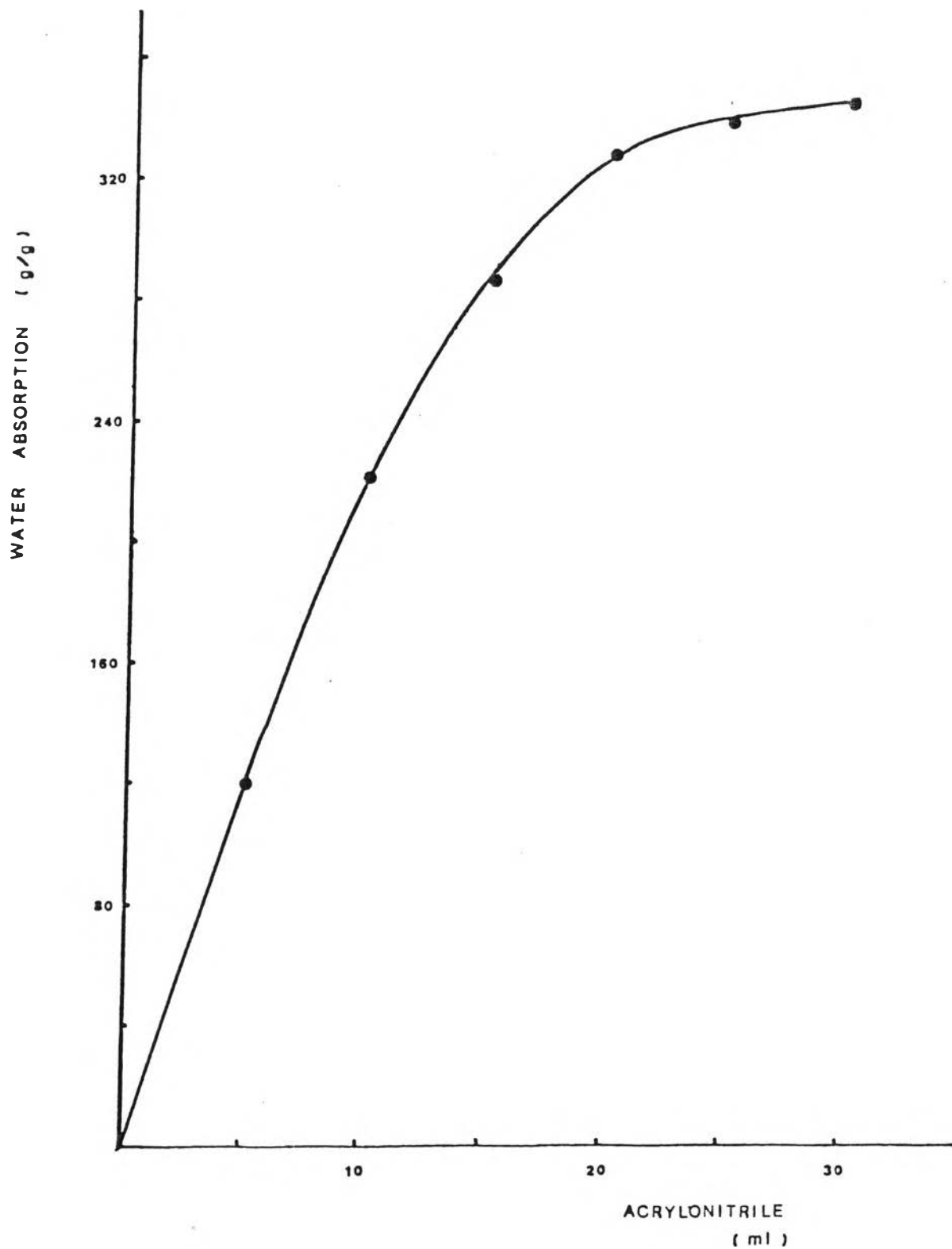


Figure 3.21 Water absorption of saponified starch-g-PAN as a function of acrylonitrile (gelatinization 80°C)

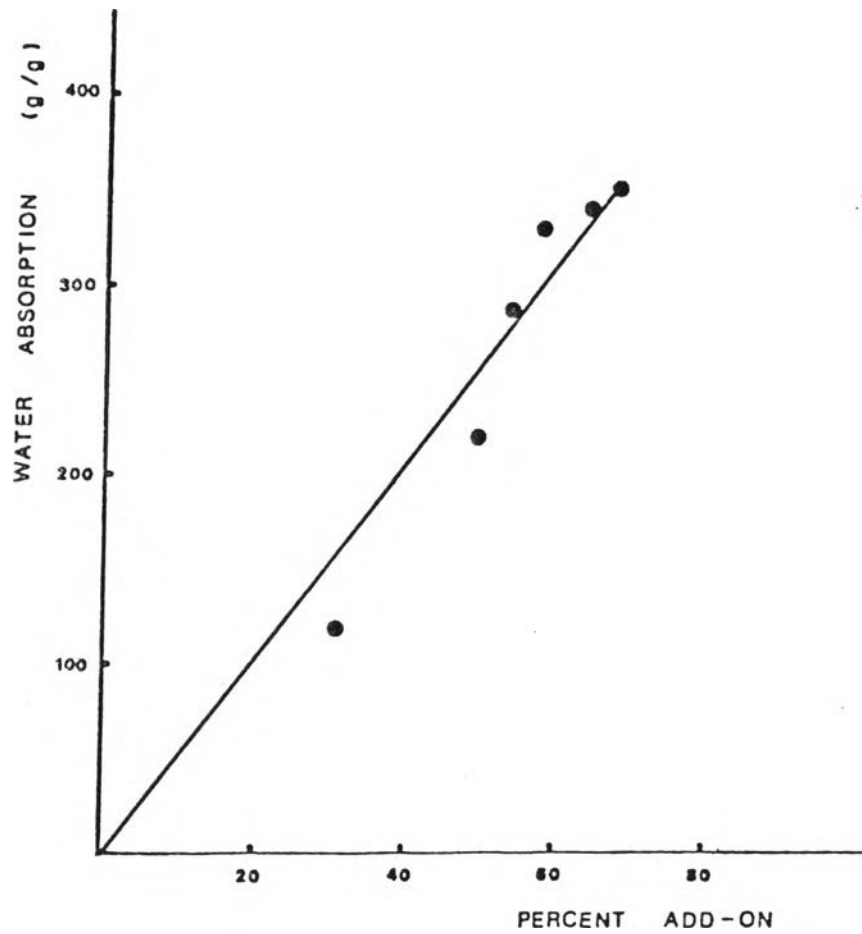


Figure 3.22 Water absorption as a function of % add-on

### 3.4 Comparative study of $\bar{M}_v$ and water absorption between 65°C and 80°C gelatinization

Table 3.11 gives the comparative data of the  $\bar{M}_v$  at a pretreatment temperature of 65 and 80°C, and Figure 3.23 shows their respective plot of  $\bar{M}_v$  as a function of the acrylonitrile concentration. The results indicate an increase in  $\bar{M}_v$  of less than 10% when the substrate was gelatinized at 80°C. Similar results were obtained by Rånby and coworkers [22] when they worked on the effect of the gelatinization temperature by grafting AN onto potato starch with Mn(III) as initiator. They explained that an increase in the MW of grafts appeared to be due to autoacceleration of polymerization caused by the diffusion-controlled termination, called the gel effect or Trommsdorf-Norrish effect [35].



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Table 3.11 Comparison of  $\overline{M}_v$  of starch-g-PAN resulting from 65 °C and 80 °C gelatinization temperatures.

Starch(g)/AN(ml)	$\overline{M}_v$	
	65 °C gelatinization	80 °C gelatinization
10: 5.0	388,500	382,600
10:10.0	465,000	501,600
10:15.0	544,800	550,300
10:20.0	566,000	600,900
10:25.0	564,000	603,700
10:30.0	568,900	604,700

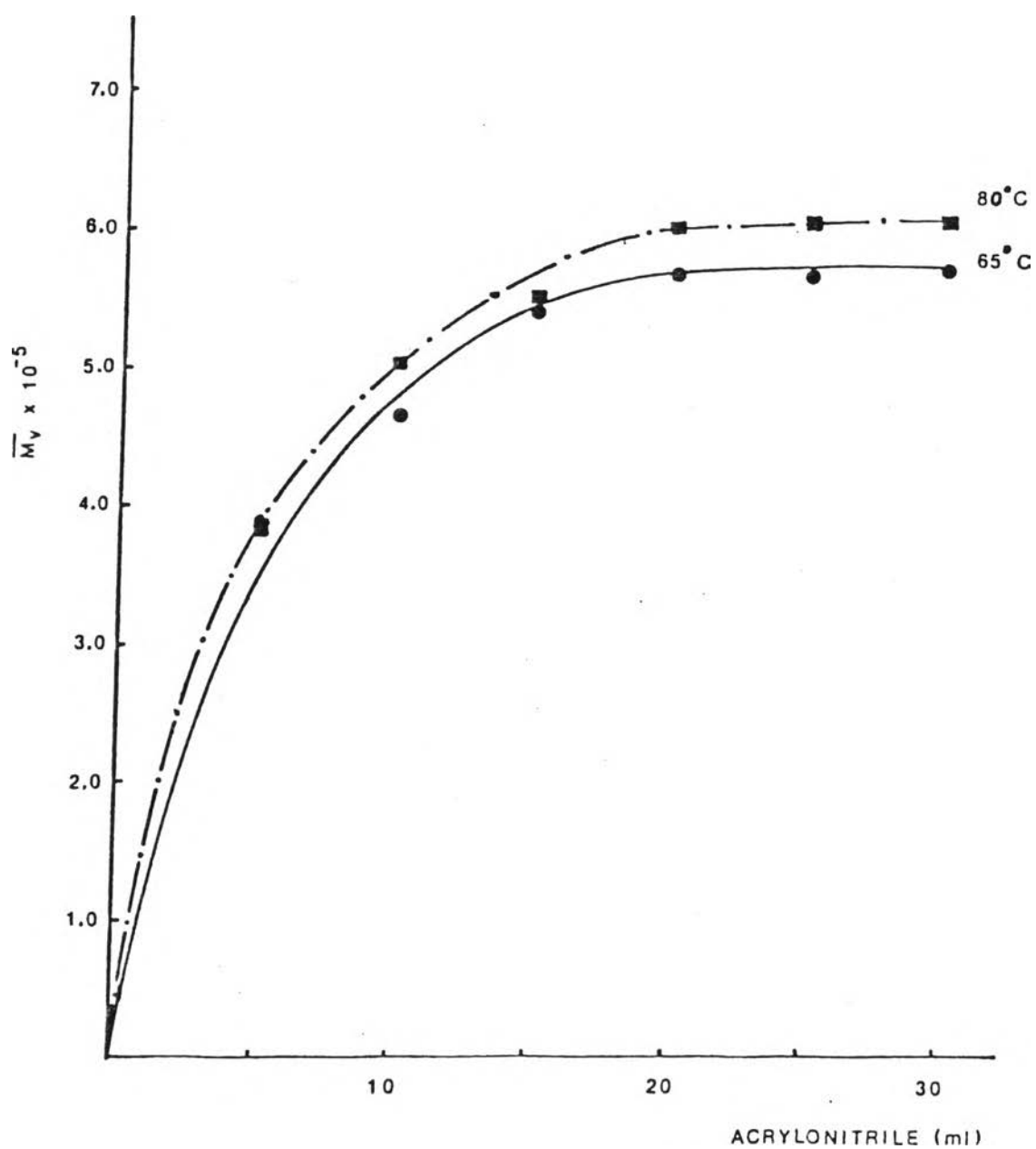


Figure 3.23 Comparison between  $\bar{M}_v$  of the two types of starch-g-PAN (gelatinization temperatures 65°C and 80°C)

During gelatinization the starch granules absorb water, increase in size, swell and gelatinize to give a viscous paste. In a viscous medium, the mobility of the propagating polymer chain is limited and so is the reactive center, and consequently the rate of termination is reduced. The paste prevents free radicals to couple during the grafting reaction thus allowing polymerization to continue leading to a higher MW. Only termination via the disproportionation mechanism is then expected. The increase in MW after pretreatment at 80 °C suggested that the viscosity of the reaction medium increased, and as a consequence slowed down the termination reaction.

Table 3.12 gives the water absorption data and shown in Figure 3.24. They indicate that the maximum water absorption at 80 °C gelatinization was dramatically higher than at 65 °C. Their water absorption plateau were 340 and 220 g/g respectively. The result of the higher water absorption can thus be correlated with a higher  $\overline{M}_v$  of starch-g-PAN. The higher the concentration of carboxylate and carboxylamide groups, the higher water absorption. Also, as mentioned earlier, the increase in ion concentration within the saponified starch-g-PAN is directly linked to the increase in osmotic pressure when the graft copolymer gets in contact with water. The higher the osmotic pressure, the higher the water absorption.

Table 3.12 Comparison of water absorption data between 65°C and 80°C gelatinization temperatures.

Starch(g)/AN(ml) ratio	Water absorption (g/g)	
	65°C gelatinization	80°C gelatinization
10: 5.0	81.7	118.5
10:10.0	162.1	220.5
10:15.0	206.6	285.3
10:20.0	220.7	327.5
10:25.0	221.4	338.2
10:30.0	221.5	344.5

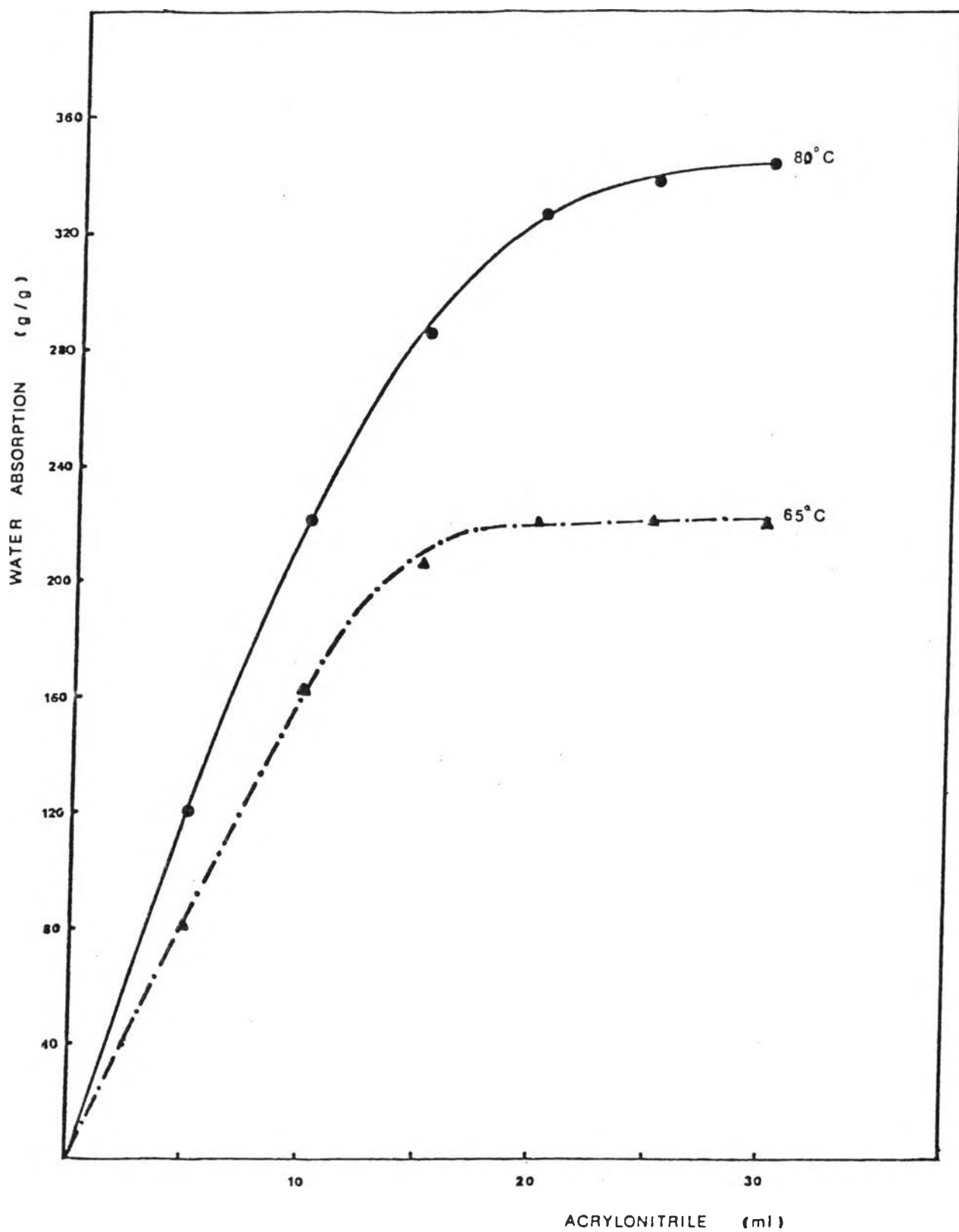


Figure 3.24 Comparison of deionized water absorptions between 65°C and 80°C gelatinization

### 3.5 Water retention in sand by mixing it with saponified starch-g-PAN

In order to see the water retention capacity in sand, saponified starch-g-PAN (65°C gelatinization temperature) was used. The water retention in sand alone was 34.71%. By mixing sand with 0.5, 1.0, 1.5, and 2.0% concentration of copolymer, the water retention of the medium increased dramatically. The data are given in Table 3.14 and illustrated in Figure 3.25. They clearly indicate that the water retention is depended on the amount of polymer used and the absorption efficiency of the different copolymers. Figure 3.25 shows that there is a linear relationship between water retention and polymer concentration. As the concentration increases, so does the water retention. Also, as the starch/AN ratio goes from 10:5.0 to 10:15.0, the water retention increases as well. The ratios 10:20.0, 10:25.0, and 10:30.0 give nearly the same retention which is indicative of the plateau previously discussed.

Table 3.13 Water retention by mixing sand with saponified starch-g-PAN (gelatinization at 65°C).

starch(g)/ AN(ml) ratio	Water retention (%)			
	0.5% polymer in sand	1% polymer in sand	1.5% polymer in sand	2% polymer in sand
10: 5.0	63.09	69.69	133.10	173.50
10:10.0	77.25	117.71	166.47	207.62
10:15.0	91.21	126.76	272.02	272.25
10:20.0	104.53	156.62	223.33	283.32
10:25.0	100.32	162.03	223.60	287.77
10:30.0	100.03	163.68	235.82	290.28

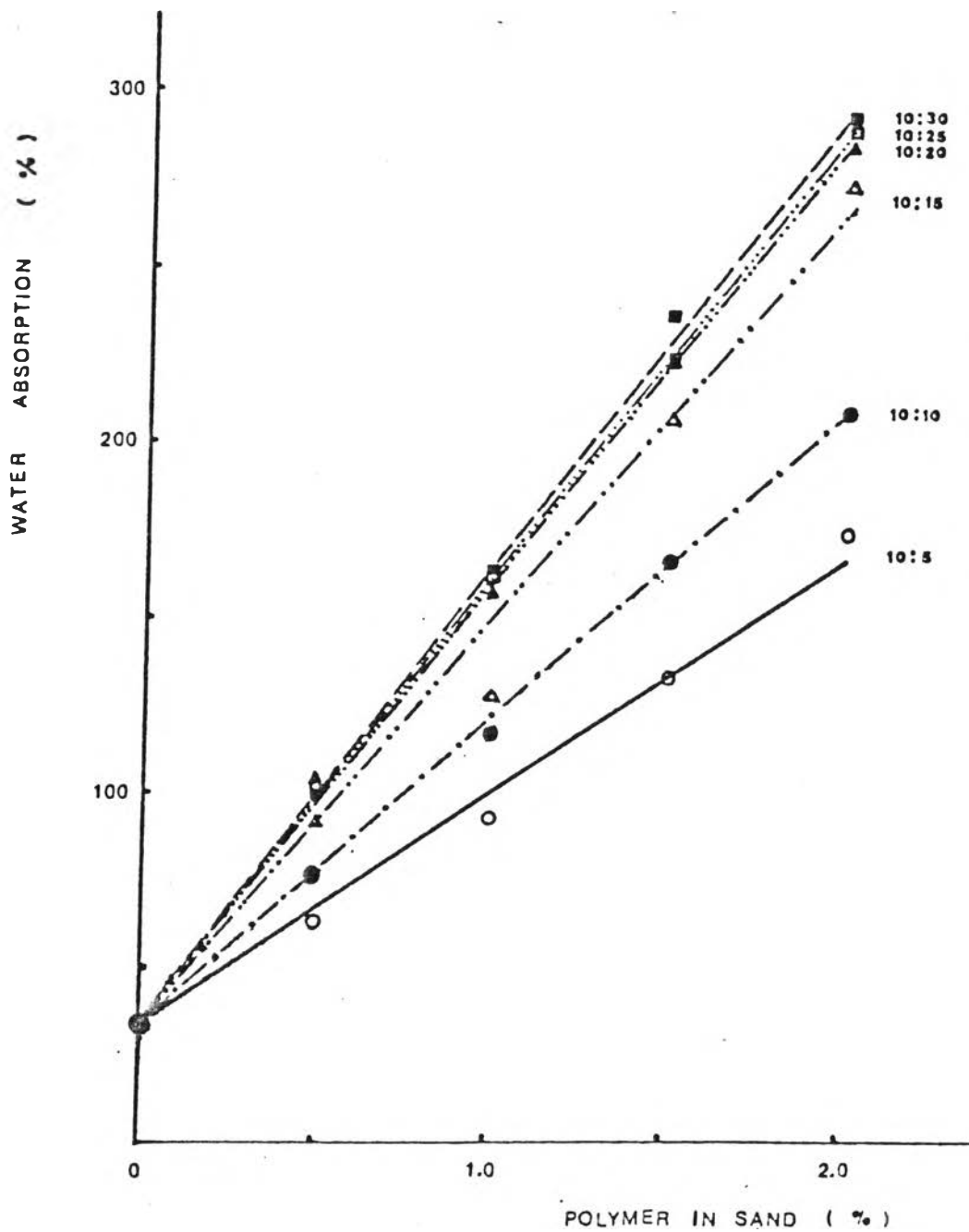


Figure 3.25 Water retention in sand by mixing with saponified starch-g-PAN