

CHAPTER IV

RESULTS and DISCUSSION

Infrared Analyses

FT-IR technique was used to follow the up polymerization, hydrolysis and copolymerization. Figures 4.1 - 4.4 show the respective IR spectra of polyacrylamide, partially hydrolyzed polyacrylamide at various degrees of hydrolysis and the reaction products after copolymerization, the partially hydrolyzed polyacrylamide with 1-vinyl-2-pyrrolidone at various degrees of hydrolysis of partially hydrolyzed polyacrylamide. Table 4.1 gives the infrared absorption of functional groups of polyacrylamide, partially hydrolyzed polyacrylamide and partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone). The infrared absorption of polyacrylamide gave the absorption bands at 3254, 3196 and 1414 - 1662 cm^{-1} , the characteristics of the $-\text{CONH}_2$ group containing in the polyacrylamide. After the hydrolysis of polyacrylamide one can observe the stretching absorption peaks of the $-\text{CONH}_2$ group that shows the weaker bands in the 3175 - 3227 cm^{-1} region (corresponding to the $-\text{NH}_2$ group) than the previous polyacrylamide spectra, the appearance of the absorption peak of the $-\text{COO}$ group at 1564, 1407 cm^{-1} and the assignment of the band in the 3227 cm^{-1} region is the bound water. The IR absorption spectrum of partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) demonstrated characteristic bands for both partially hydrolyzed polyacrylamide and poly(1-vinyl-2-pyrrolidone). The assignment of the band in the 3300 cm^{-1} region to bound water was made according to similar absorption in the spectrum of partially hydrolyzed polyacrylamide. Other bands include the C-H stretch vibration at 2942 cm^{-1} . Carbonyl amide bands occurring as a strong

peak near 1664 cm^{-1} close to the frequency observed in spectrum of poly(1-vinyl-2-pyrrolidone). Methylene deformation peaks in the $1323 - 1444\text{ cm}^{-1}$ region have the same pattern as those in the spectrum of poly(1-vinyl-2-pyrrolidone). The band at 1291 cm^{-1} represents the C - N stretching mode of 1-vinyl-2-pyrrolidone monomers units.



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Table 4.1 The Infrared Absorption of Functional Groups in Polyacrylamide(PAM), Partially Hydrolyzed Polyacrylamide and Partially Hydrolyzed Poly(acrylamide-co-1-Vinyl-2-Pyrrolidone).

Polyacrylamide(PAM)		Partially Hydrolyzed Polyacrylamide (HPAM)		HPAM-1-vinyl-2-pyrrolidone Copolymer	
Wave number	Assignment	Wave number	Assignment	Wave number	Assignment
2940 (w) 1452 (m)	C-H stretching of CH ₂	2938 (w) 1452 (m)	C-H stretching of CH ₂	2942 (w) 1444 (m)	C-H stretching of CH ₂
3254 and 3196 (s) 1662 (vs) 1414 (m)	-CONH ₂	3227 and 3175 1673 (vs) 1407 (m)	-CONH ₂	3363 and 3300 1644 (vs) 1409 (m)	-CONH ₂
1352 (w)	-CH	1326 (w)	-CH	1323 (w)	-CH
-	-	> 3227 (sh)	H ₂ O	> 3300 (sh)	H ₂ O
-	-	1673 (vs)	-COOH	1664 (vs)	-COOH
-	-	1564 (m) 1407(m)	-COO	1563 (m) 1409 (m)	-COO
1291	C-N stretching	-	C-N stretching	1291	C-N stretching

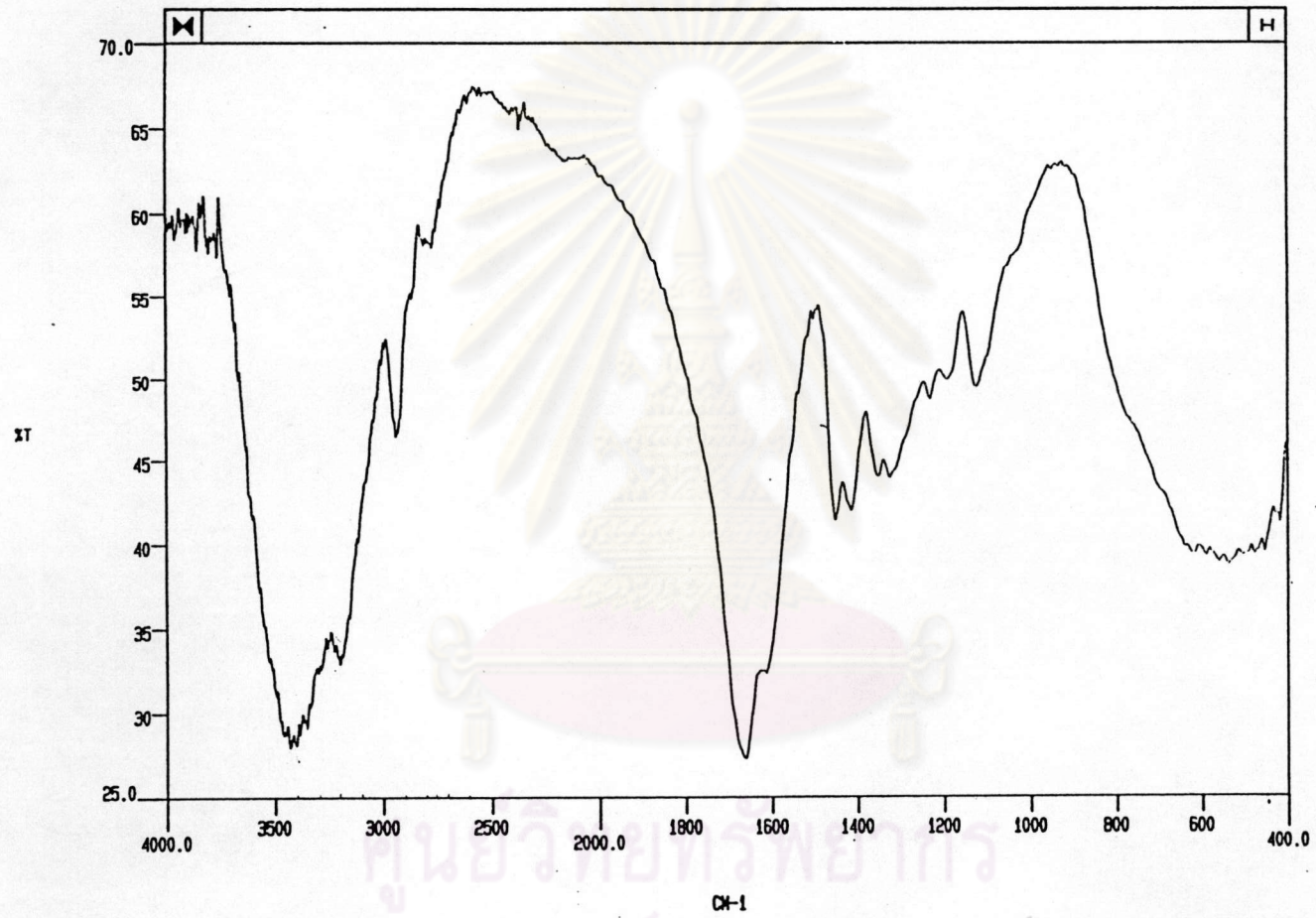


Figure 4.1 Infrared spectrum of polyacrylamide

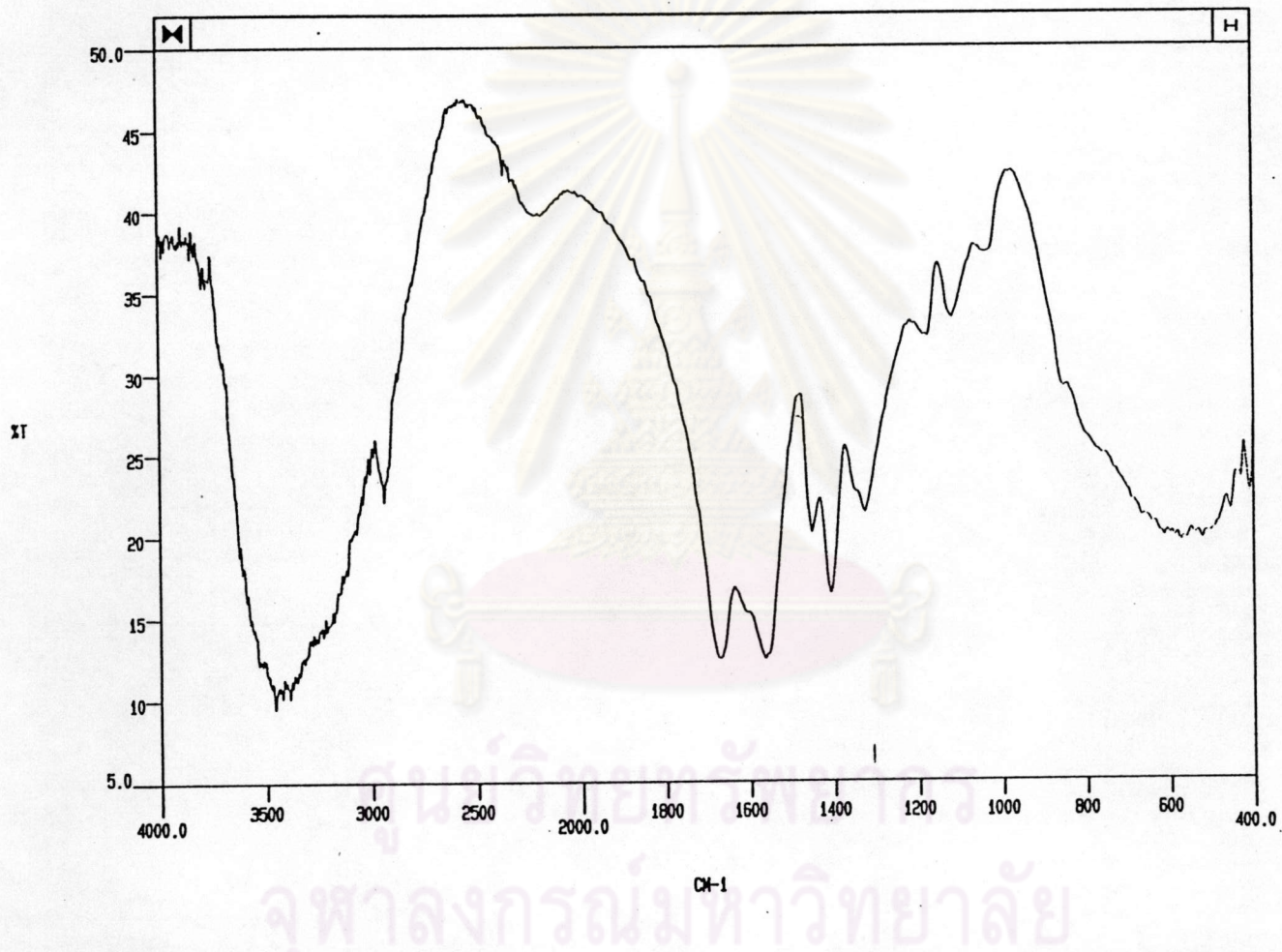


Figure 4.2 Infrared spectrum of 71% partially hydrolyzed polyacrylamide(71% HPAM)

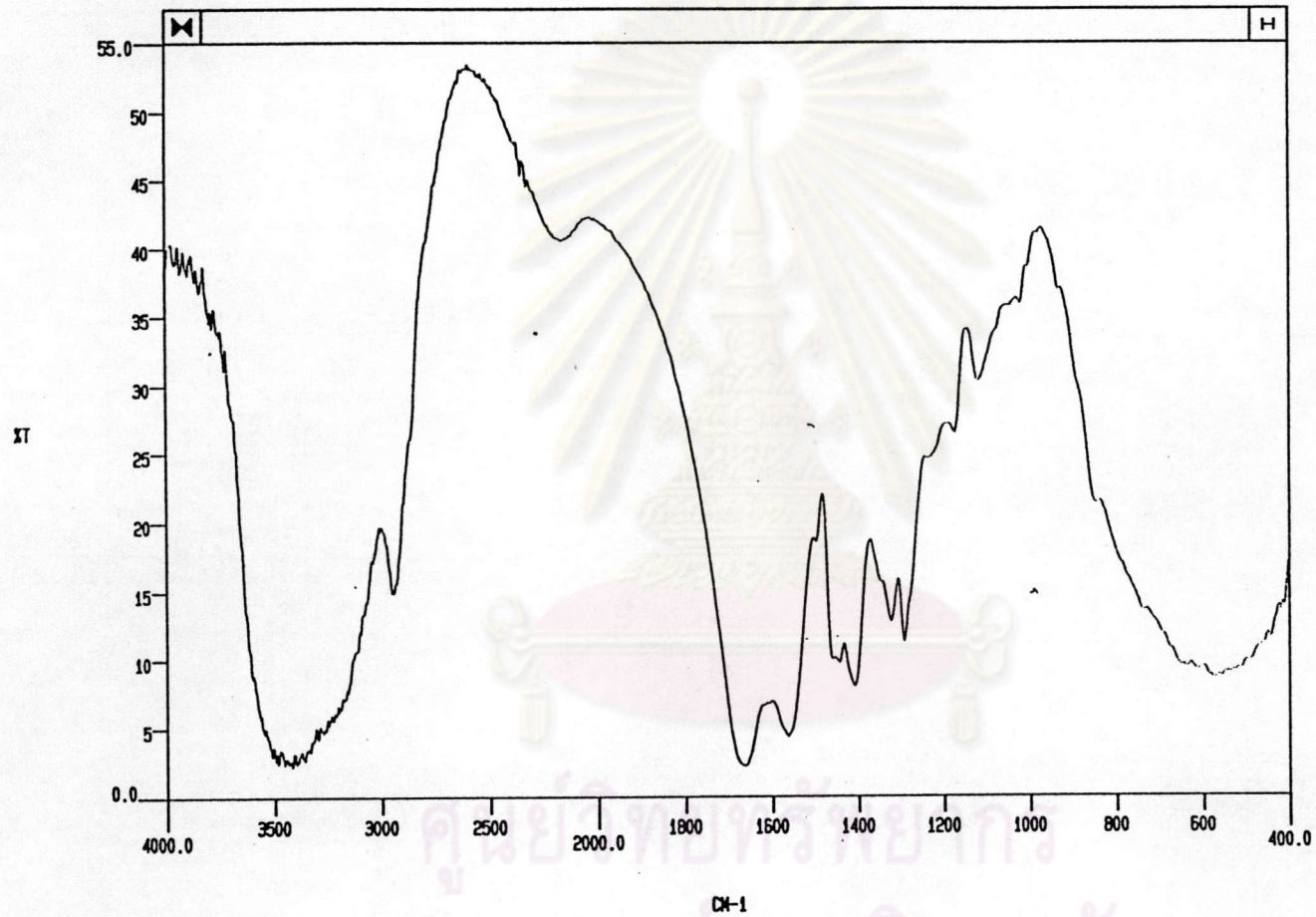


Figure 4.3 Infrared spectrum of 71% partially hydrolyzed poly(acrylamide(HPAM)-co-1-vinyl-2-pyrrolidone)

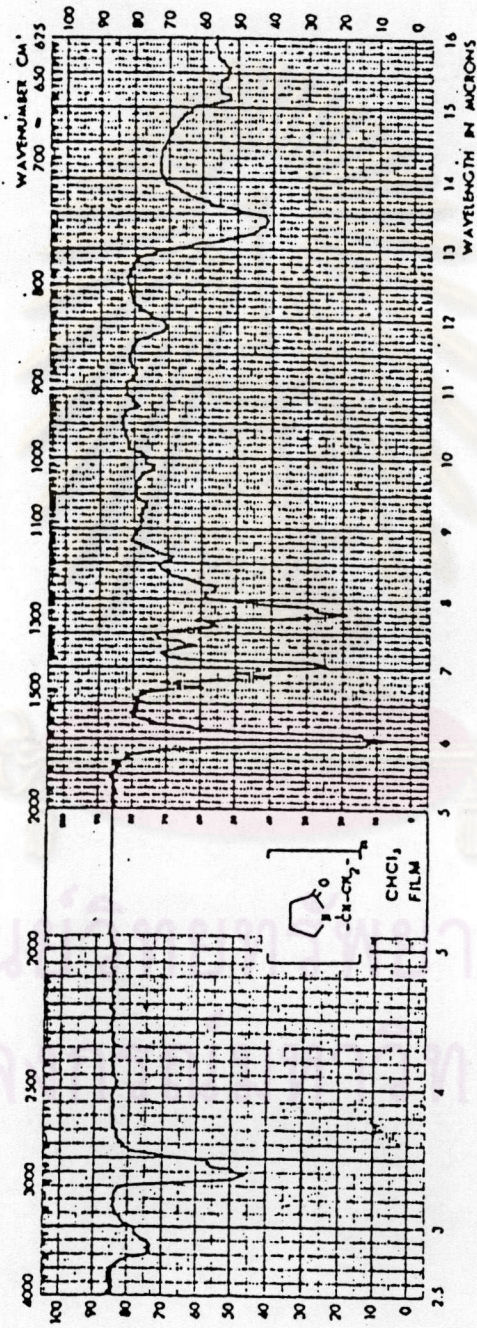
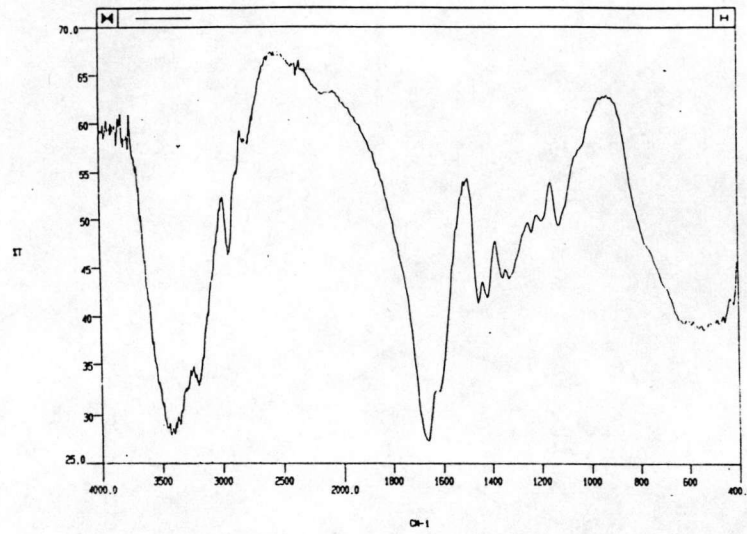
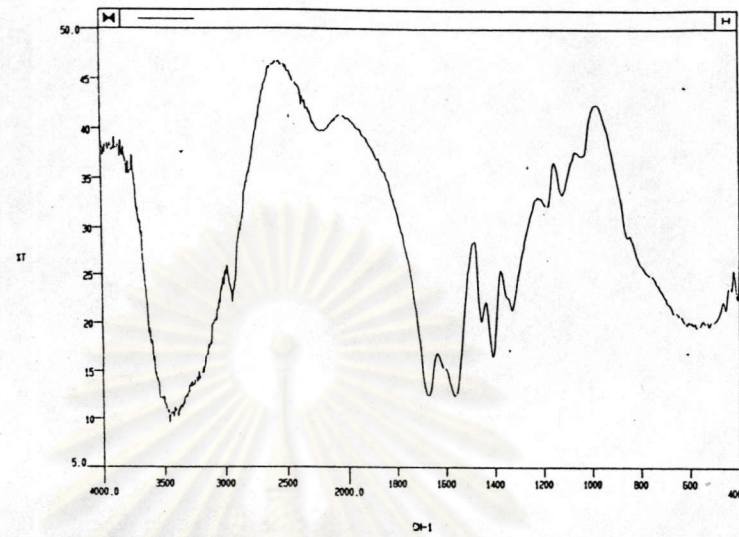


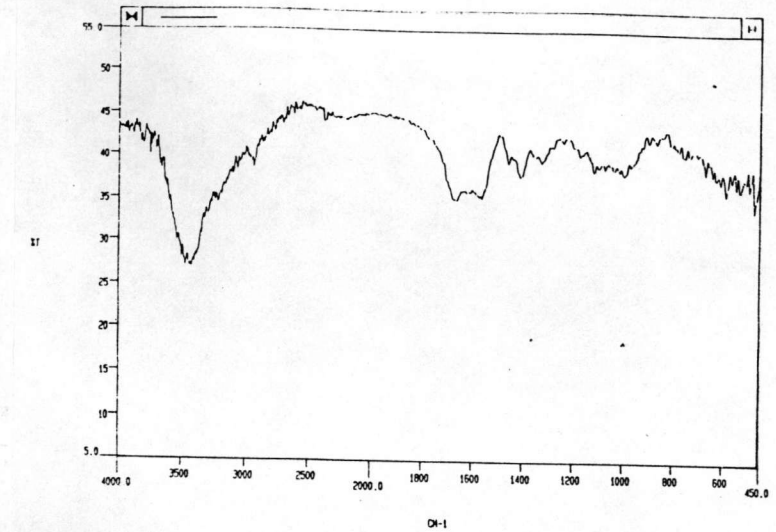
Figure 4.4 Infrared spectrum of poly(vinyl pyrrolidone)



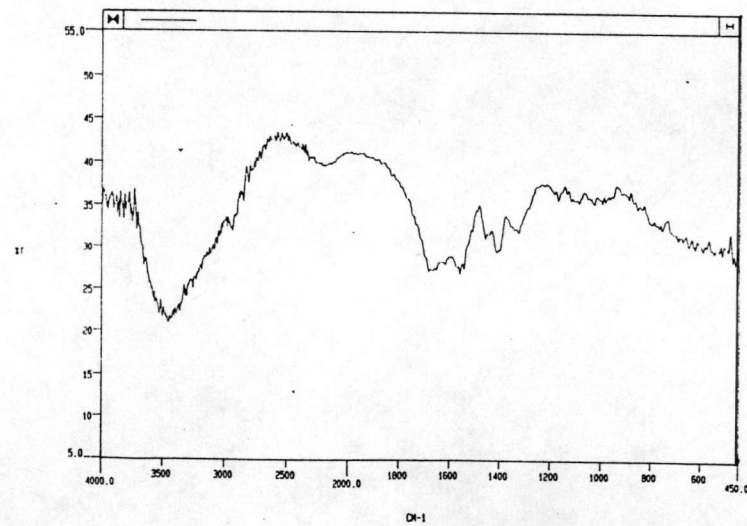
(a)



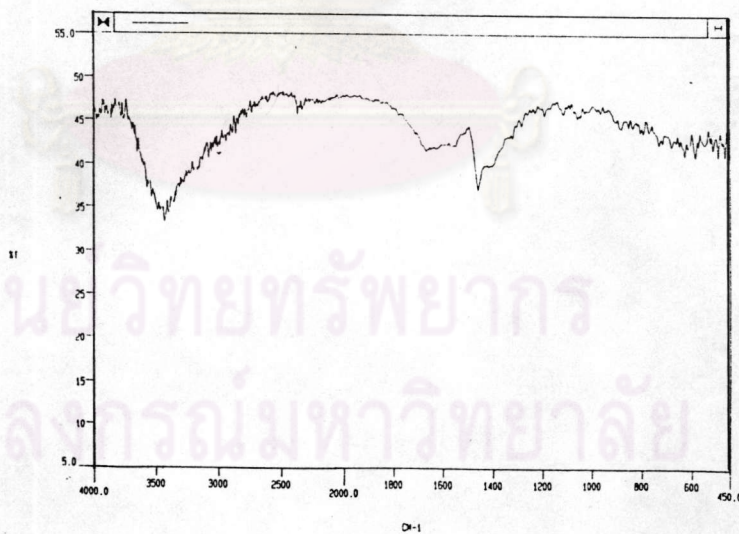
(b)



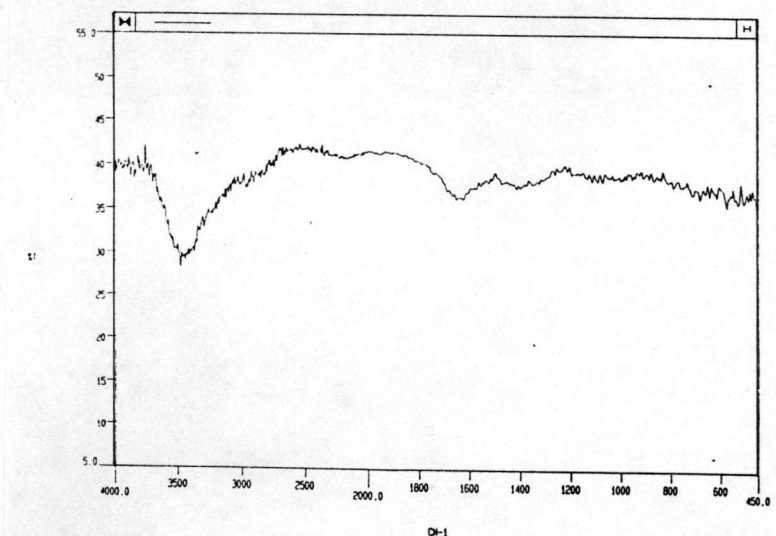
(c)



(d)



(e)



(f)

Figure 5.5 Infrared spectrum of (a) PAM (b) 63% HPAM (c) 71% HPAM (d) 76% HPAM (e) 80% HPAM (f) 84% HPAM

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Polymerization of Acrylamide by Gamma Irradiation

1. Effect of Total Dose on Polymerization

The result of the effect of total dose(kGy) on the polymerization of acrylamide by the gamma rays at a fixed dose rate of 1.19×10^4 Gy/h is presented in terms of the conversion of monomer(%) as shown in Table 4.2 and Figure 4.6.



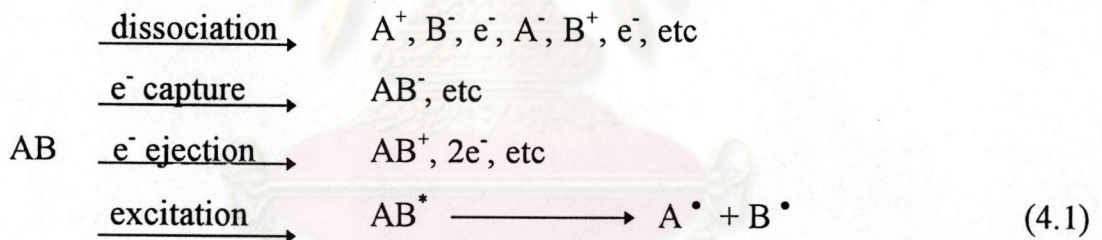
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Table 4.2 Effect of Total Dose(kGy) on Polymerization of Acrylamide at a Fixed Dose Rate of 0.1990 kGy/min.

Total Dose (kGy)	Conversion (%)
0.1	-
0.2	-
0.3	26
0.4	29
0.5	44
0.6	50
0.7	63
0.8	67
0.9	73
1.0	79
1.1	82
1.2	85
1.3	88
1.4	98
1.5	93
1.6	93
1.7	92
1.8	92
1.9	92
2.0	91

Table 4.2 and Figure 4.6 show the correlation between the total dose and percent conversion. The curve shows a continuous increase in percent conversion of the monomer as the amount of total irradiation dose increases. The highest homopolymer occurred at the total irradiation dose of 1.4 kGy. Higher total dose decreases the percent conversion slowly. An increase in the total dose enhances the formation of radicals in the reaction mixture: monomer, acetone and water. All molecules are activated to induce a higher conversion for homopolymer formation. Nonetheless, a greater extent of the homopolymer formation, occurs at the optimum total dose.

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:



The total irradiation dose at 1.4 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.

2. Effect of Dose Rate on Polymerization of Acrylamide by Gamma Irradiation

The experimental data of the effect of dose rate(Gy/h) on polymerization of acrylamide is presented in terms of the conversion of monomer(%) as shown in Table 4.3 and Figure 4.7.

Table 4.3 Effect of Dose Rate(kGy/min) on Polymerization of Acrylamide.

Dose Rate(kGy/min)	Conversion(%)
3.60×10^3	90
5.34×10^3	91
1.19×10^4	98

The curve shows a continuous increase in percent conversion of the monomer as the amount of dose rate increases. An increase in the dose rate enhances in the density of primary events that are involved. The yields of the stable reaction products should increase or decrease, depending on whether they are formed by reactions with molecular or radical primary products.

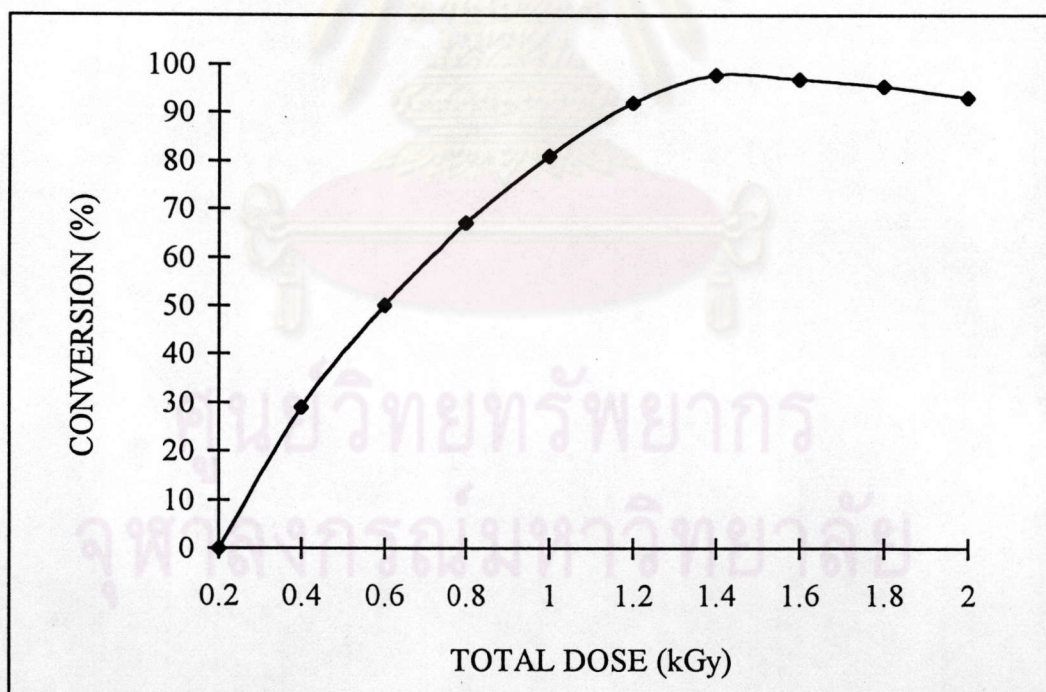


Figure 4.6 Effect of total dose(kGy) on percent conversion

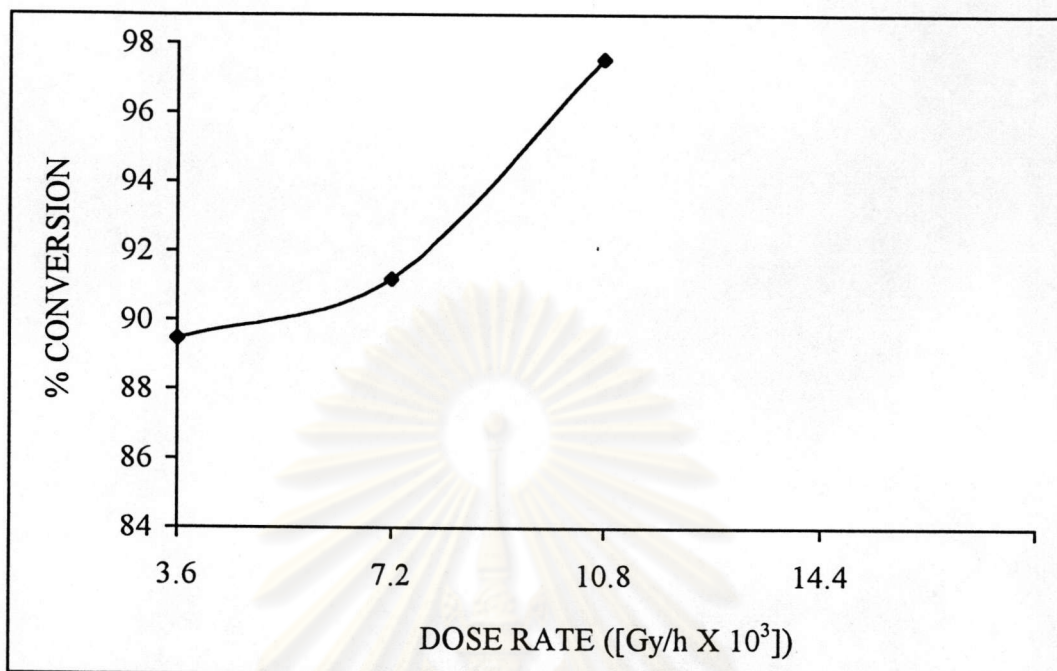


Figure 4.7 Effect of dose rate(Gy/h) on percent conversion.

3. Effect of Concentration of Acrylamide on Polymerization.

The effect of concentration of acrylamide as a monomer for polymerization is indicated in Table 4.4 and Figure 4.8.

Table 4.4 Effect of Concentration of Acrylamide(M) on Polymerization.

Concentration(M)	Conversion(%)
0.5	61
1.0	78
1.5	85
2.0	91
2.5	98
3.0	91
3.5	91

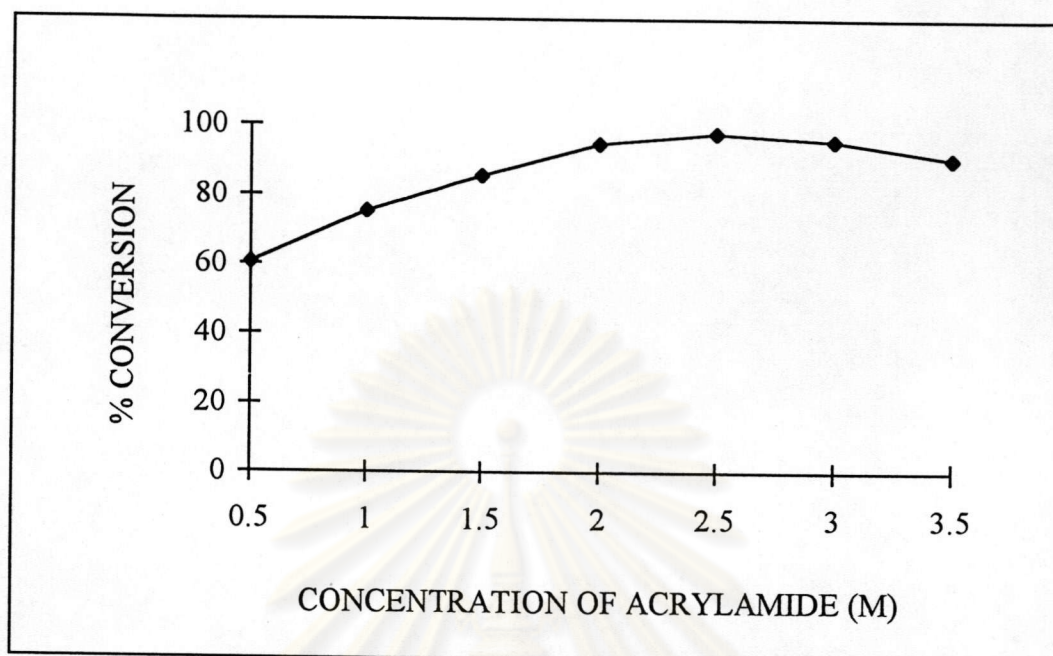
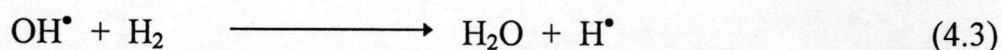
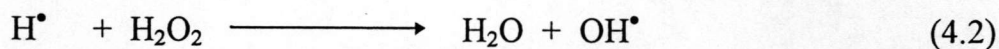


Figure 4.8 Effect of concentration of acrylamide(M) on percent conversion.

According to the results of the concentration of acrylamide, as the concentrations of the acrylamide ranging from 0.5 to 2.0M, it was found that percent conversion was increased proportionally to the concentration of monomer([M]). The highest homopolymer occurred at the concentration of 2.5M. Beyond 2.5 to 3.0M percent conversion dropped as the concentrations of the monomer further increased. At concentrations above 2M, the reaction mixture becomes very viscous after the conversions of 5 to 10 % and it is likely that the "gel effect" is operative at this stage. The gel effect would account for the acceleration period.

The $G(\text{H}_2\text{O}_2)$ first increases with the monomer concentration, up to 2.5M solution, and thereafter it steadily decreases. The increase of $G(\text{H}_2\text{O}_2)$ with the concentration of monomer was ascribed to the fact that the acrylamide traps H and OH radicals with an increasing efficiency and thus prevents back reactions such as:



on the other hand, the decrease of $G(\text{H}_2\text{O}_2)$ at the monomer concentrations above 2.5M was believed to result from the trapping of precursors of “molecular” hydrogen peroxide.

Hydrolysis of Polyacrylamide

The degree of hydrolysis as functions of temperature($^\circ\text{C}$), reaction time(h) and concentration of NaOH(%w/v) is considered as the important attribute to the subsequent copolymerization, which is presented in Table 4.5. Each parameter affecting the degree of hydrolysis is illustrated in Figures 4.9 - 4.11.

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Table 4.5 Degree of Hydrolysis as Functions of Temperature($^{\circ}\text{C}$), Reaction Time(h) and Concentration of NaOH (% w/v)

Reaction Time(h)	Concentration NaOH (% w/v)	Degree of Hydrolysis(%) at Temperature($^{\circ}\text{C}$)			
		50	60	70	80
1	5	68	71	72	72
	10	76	72	71	71
	15	76	73	73	73
	20	73	76	76	76
2	5	63	71	75	76
	10	76	76	72	72
	15	77	75	80	80
	20	74	83	80	78
3	5	73	72	76	75
	10	77	76	76	76
	15	78	76	74	73
	20	73	79	84	84
4	5	74	73	76	75
	10	78	77	74	71
	15	79	75	75	72
	20	73	79	85	84

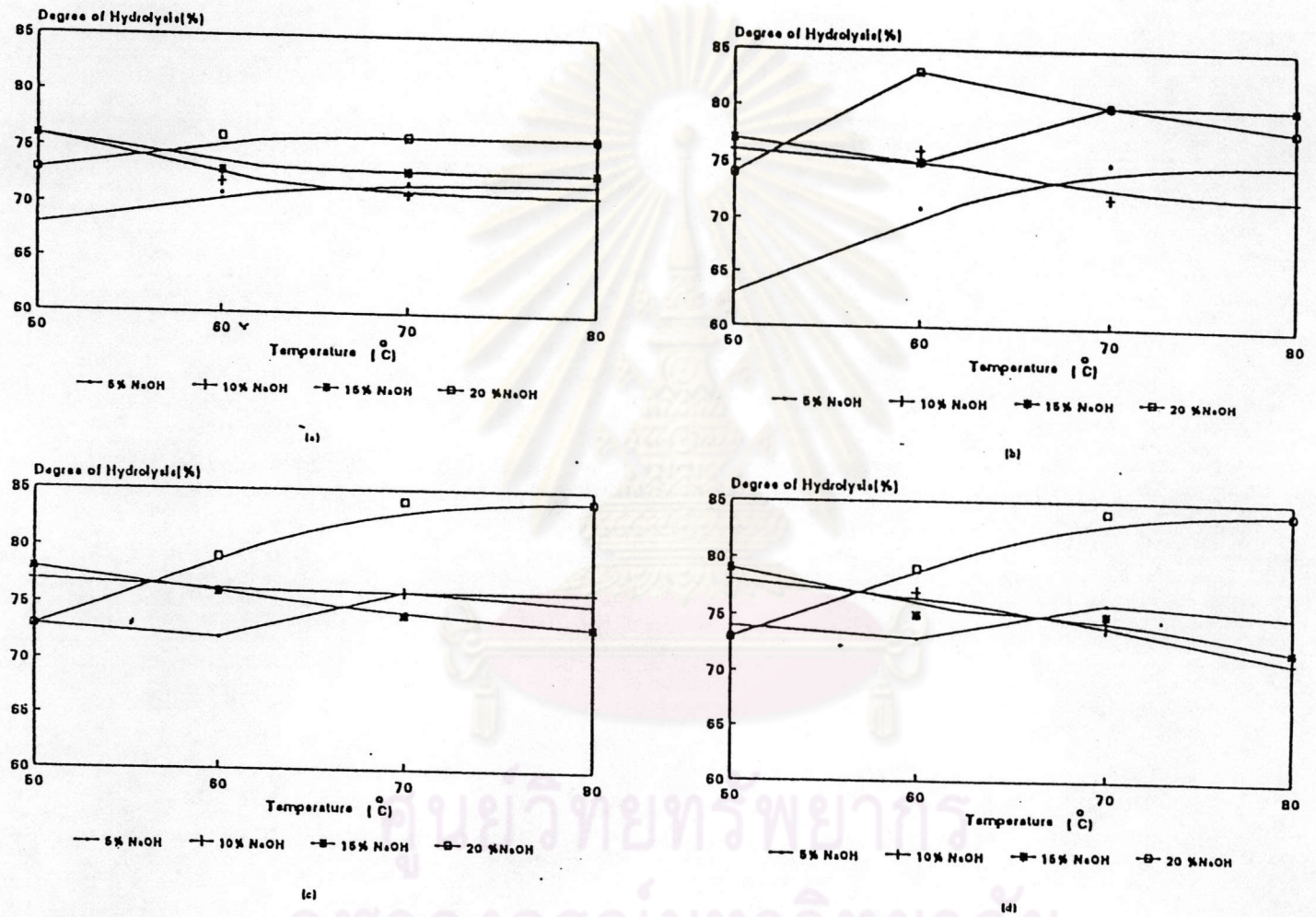
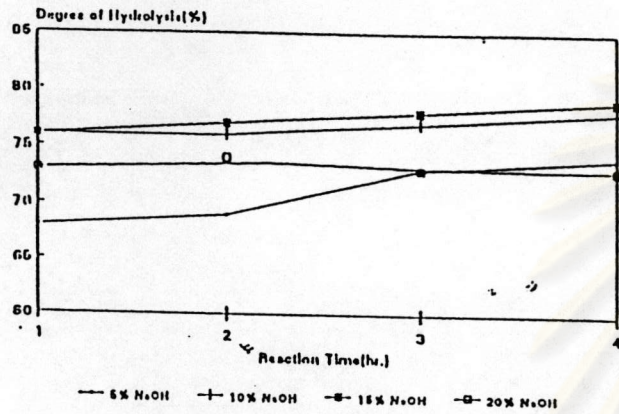
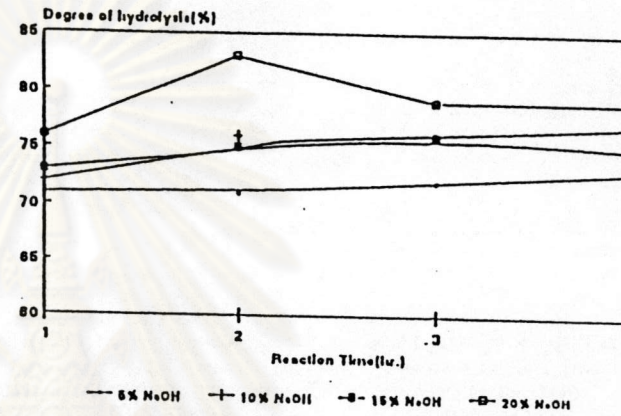


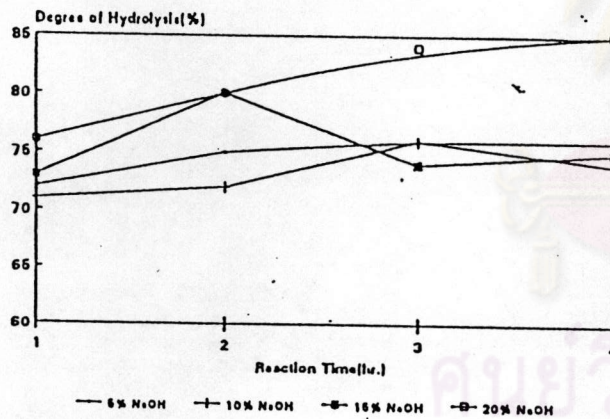
Figure 4.9 Effect of temperature on degree of hydrolysis at the reaction conditions: reaction time (a) 1 h (b) 2 h (c) 3 h (d) 4 h.



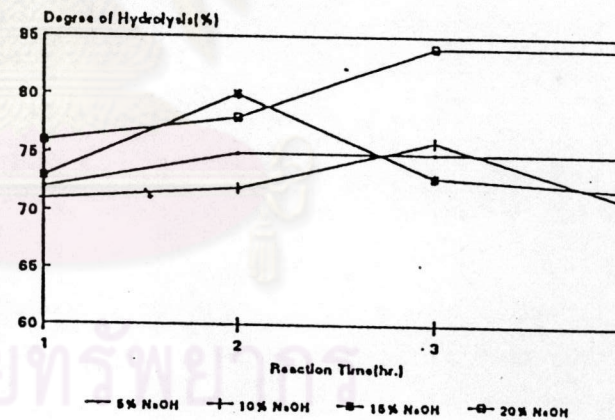
(a)



(b)

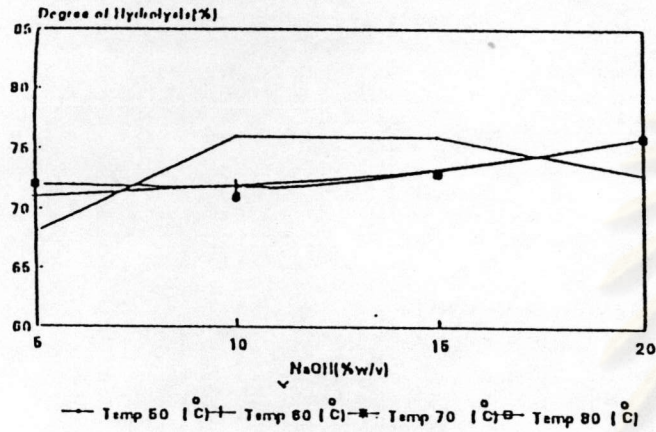


(c)

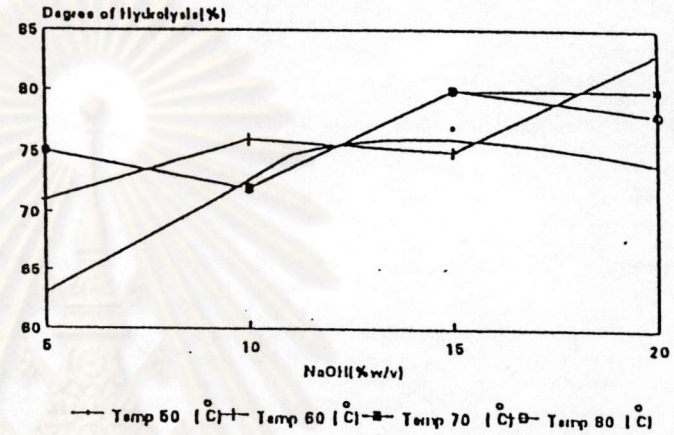


(d)

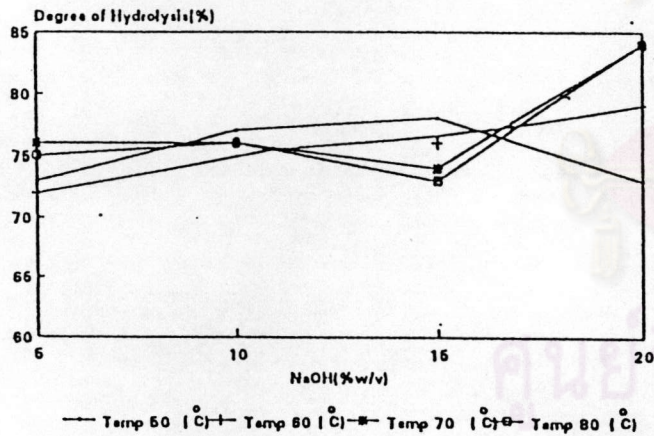
Figure 4.10 Effect of reaction time on degree of hydrolysis at the reaction conditions: temperature (a) 50 °C (b) 60 °C (c) 70 °C (d) 80 °C.



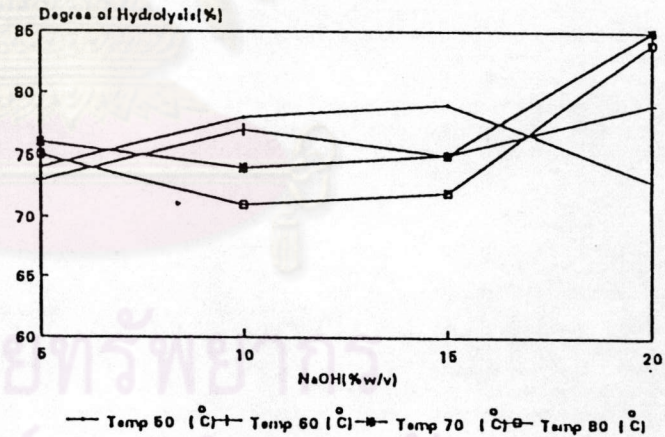
(a)



(b)



(c)

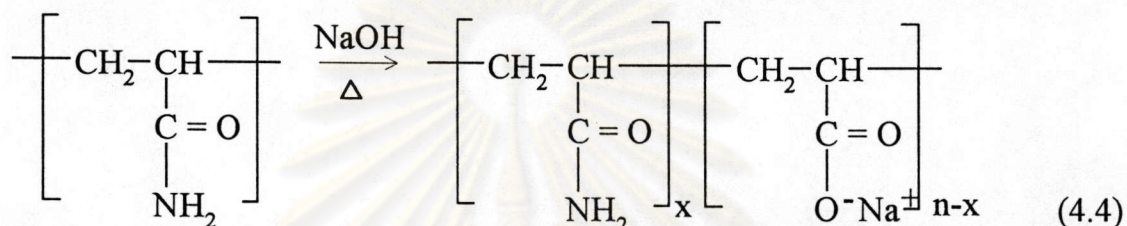


(d)

Figure 4.11 Effect of sodium hydroxide on degree of hydrolysis at the reaction conditions: reaction time (a) 1 h (b) 2h (c) 3 h. (d) 4 h.

1. Relationship between Temperature and Degree of Hydrolysis

Figure 4.12 shows a continuous increase in the degree of hydrolysis as the temperature increases. The higher the temperature, the more the changes in the amide groups along the polyacrylamide backbone to the carboxylate group of the hydrolyzed polyacrylamide through the following chemical reaction:



2. Relationship between Reaction Time and Degree of Hydrolysis.

The experimental data for the effect of reaction time on the degree of hydrolysis of polyacrylamide are given in Figure 4.13. Polyacrylamide undergoes an extensive hydrolysis at longer reaction times.

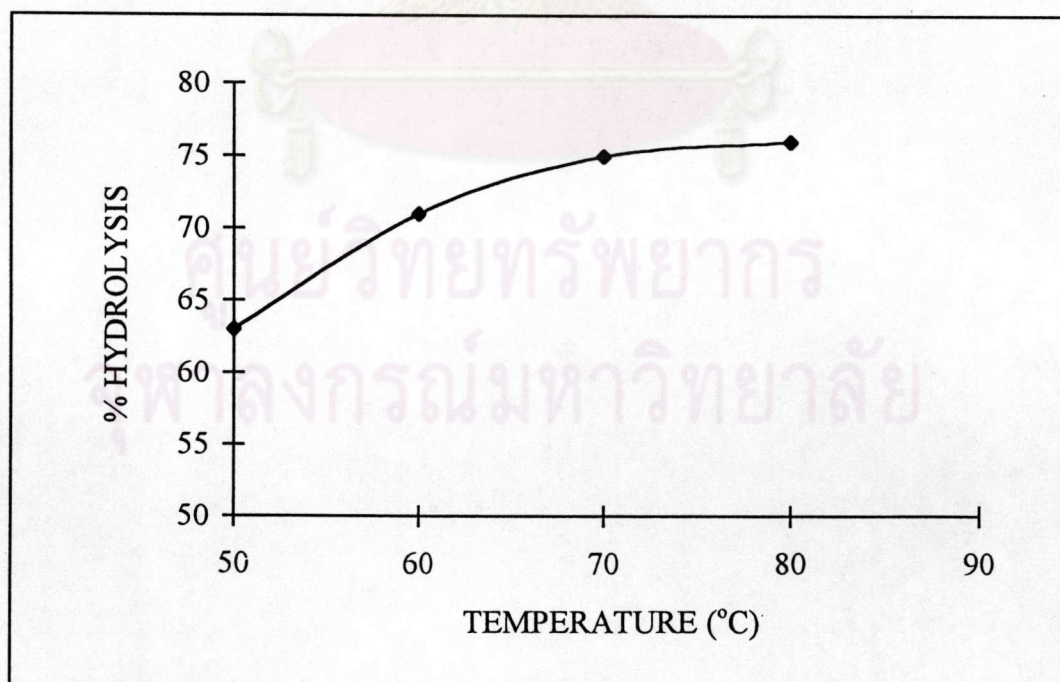


Figure 4.12 Effect of temperature on degree of hydrolysis at reaction time 2 h and 5% NaOH(w/v).

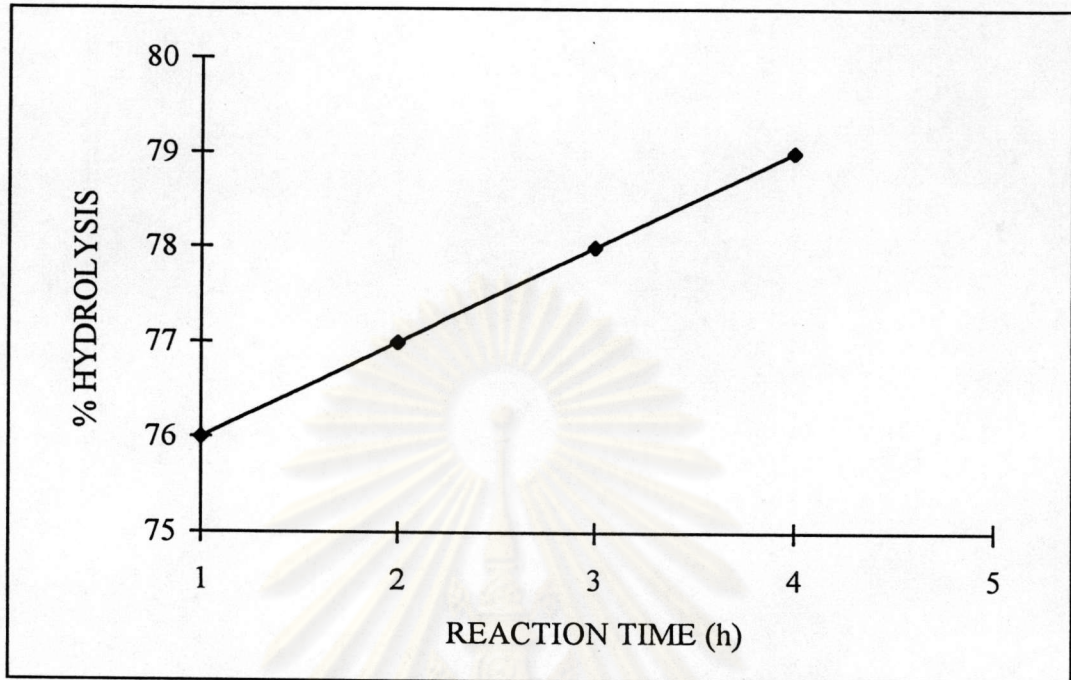


Figure 4.13 Effect of reaction time(h) on degree of hydrolysis at temperature 50 °C and 15% NaOH(w/v).

3. Relationship between the Concentration of Sodium Hydroxide and the Degree of Hydrolysis.

Figure 4.14 also shows that the degree of hydrolysis increased with increasing concentration of sodium hydroxide. The higher the concentration of sodium hydroxide, the more the changes in the amide groups along the polyacrylamide backbone to the carboxylate group of the hydrolyzed polyacrylamide.

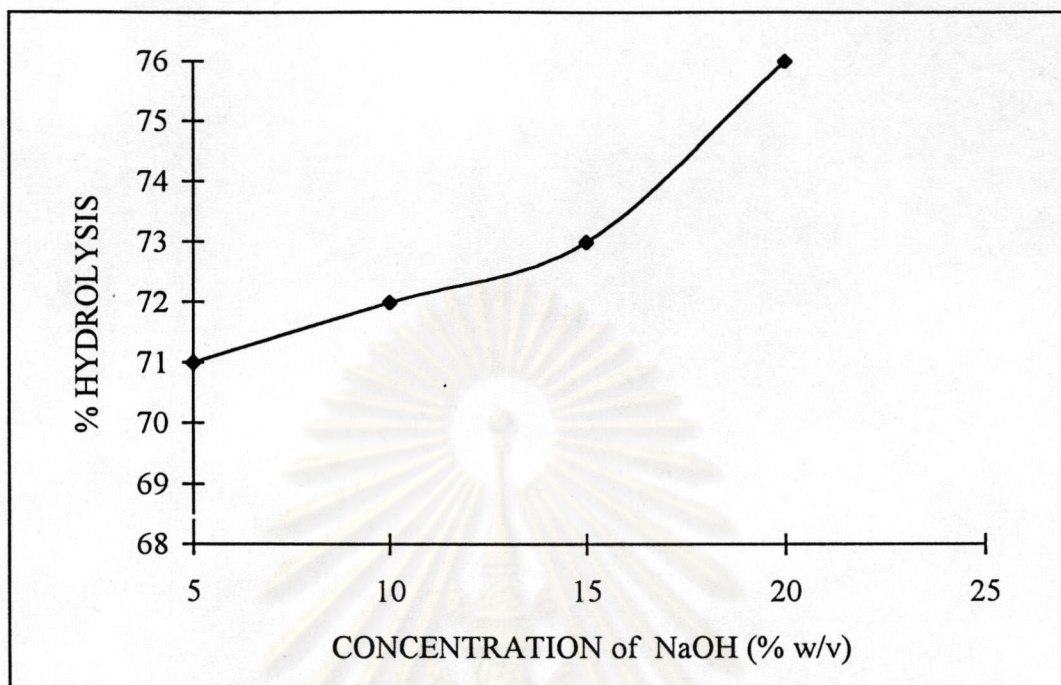


Figure 4.14 Effect of concentration of sodium hydroxide at condition: reaction time 1 h and temperature 60°C.

4. Relationship between Quantity of Polyacrylamide and the Degree of Hydrolysis.

The effect of the quantity of polyacrylamide on degree of hydrolysis is given in Table 4.6. It is apparent from Table 4.6 that the degree of hydrolysis increased with increasing the quantities of polyacrylamide up to 5 g. When the quantity of polyacrylamide higher than 5 g, the degree of hydrolysis is unchanged.

Table 4.6 Effect of the Quantities of Polyacrylamide on degree of Hydrolysis at: Reaction Time 3 h, 70°C and 20% NaOH(w/v)

Polyacrylamide(g)	Degree of Hydrolysis(%)
1	79
3	80
5	84
7	84
9	84

Copolymerization of Partially Hydrolyzed Polyacrylamide(HPAM) and 1-Vinyl-2-Pyrrolidone by Gamma Irradiation

1. Effect of Total Dose on Copolymerization.

The experimental data for the effect of total dose(kGy) on the copolymerization of the partially hydrolyzed polyacrylamide(HPAM) with 1-vinyl-2-pyrrolidone by gamma irradiation at a fixed dose rate of 1.19×10^4 Gy/h is presented in terms of the conversion of monomer(%) and the water absorption (g/g) as show in Table 4.7, Figures 4.15 and 4.16.

Table 4.7 Effect of Total Dose(kGy) on Copolymerization of Partially Hydrolyzed Polyacrylamide(HPAM) with 1-Vinyl-2-Pyrrolidone.

Total Dose(kGy)	Conversion(%)	Water Absorption(g/g)
8	37	801
9	59	896
10	79	950
11	75	755
12	72	730

1.1 Relationship between Total Dose and the Conversion of Monomer.

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 phenonema can be induced, which have been memtioned earlier in Chapter II.

The Compton process plays an important attribute to the interaction between γ -rays and the chemicals in the current research. The current polymerization reactions are believed to occur predominantly through free radical process with the minimum participation of ions. The presence of water as a reaction medium and the reaction temperature at about $30 \pm 1^\circ\text{C}$ has previously led us to believe that the roles of ions in these processes were suppressed. Therefore, all the explanations below were based on the role of free radical polymerization.

Table 4.7 and Figure 4.15 show the correlation between the total dose and the conversion of monomer. The amount of conversion of monomer varied from 37 to 79% depending on doses. The highest conversion of the monomer occured at the total irradiation dose of 10 kGy; the conversion of monomer increased with increasing the amounts of total irradiation dose up to 10 kGy. Higher than 10 kGy, the conversion of the monomer decreased. To optimize the conversion of a monomer with the minimum of contaminating homopolymer, there are a number of conditions, which need to be met. Most importantly, the yield of radicals from radiolysis of polymer (G value) must be, as much as possible, in excess of that from the monomer. Thus the copolymerization of partially hydrolyzed polyacrylamide(HPAM) with 1-vinyl-2-pyrrolidone would be reasonably favored. This suggests that the higher irradiation dose gave a large amount of radiolysis products (in the absence of oxygen): H^\bullet , OH^\bullet and of which $G(\text{H}^\bullet)$, $G(\text{OH}^\bullet)$ and $G(\text{e}^-_{\text{aq}})$ are 0.55, 2.8 and

2.7 at pH 4 - 7, respectively, which initiated homopolymerization rather than copolymerization reaction(3). The H^\bullet and OH^\bullet are the frequently chain transfer species to growing chains which consequently terminate the copolymerization reaction. The total irradiation dose at 10 kGy is thus just an optimum dose to generate the least amount of H^\bullet , OH^\bullet and e^-_{aq} for chain transfer of homopolymer growing chains and thus increase in radiolysis products, less likely cationic species due to the existence of water, and most probably free radicals with increasing the total irradiation dose. All the monomers were possibly used up for both the homopolymer formation and copolymerization reaction under the influence of the dose. 1-vinyl-2-pyrrolidone molecules were activated to induce higher conversion to copolymers.

1.2 Relationship between Total Dose and Water Absorption.

The experimental data in Table 4.7 show that at the total dose of 10 kGy, the highest water absorption is obtained. The highest water absorption can be thus be correlated with the highest conversion of monomer and the lowest percent homopolymer.

2. Effect of Dose Rate on Copolymerization.

The effect of dose rate(Gy/h) on the copolymerization of partially hydrolyzed(HPAM)-1-vinyl-2-pyrrolidone by gamma rays at a fixed total dose of 10 kGy is presented in terms of the conversion of monomer(%) and the water absorption(g/g) as shown in Table 4.8, and Figures 4.17 - 4.18.

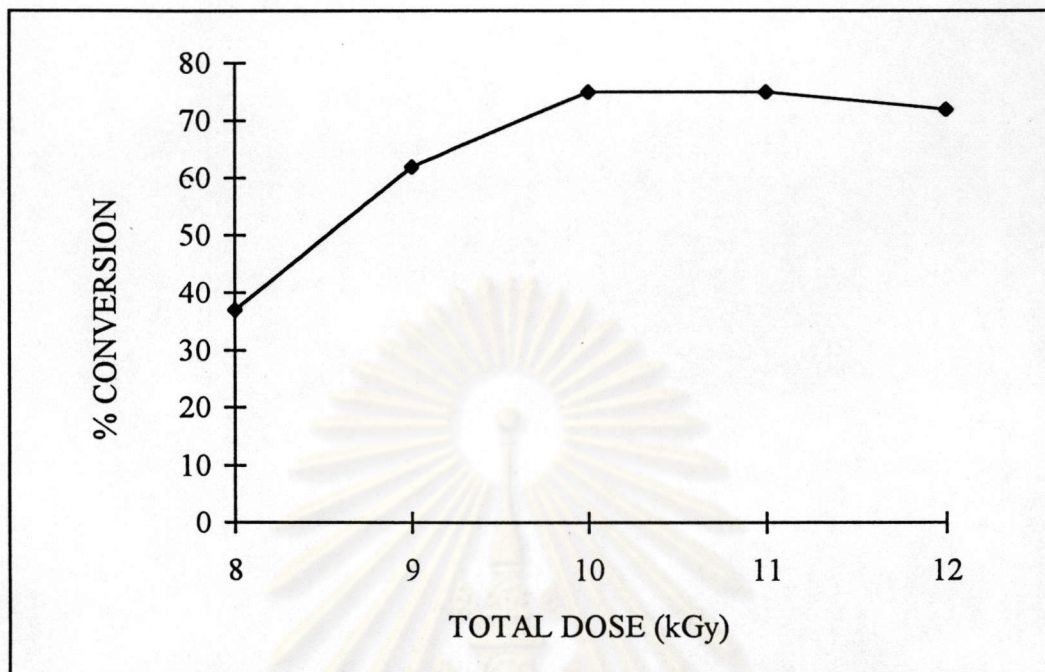


Figure 4.15 Effect of total dose(kGy) on percentage conversion of monomer.

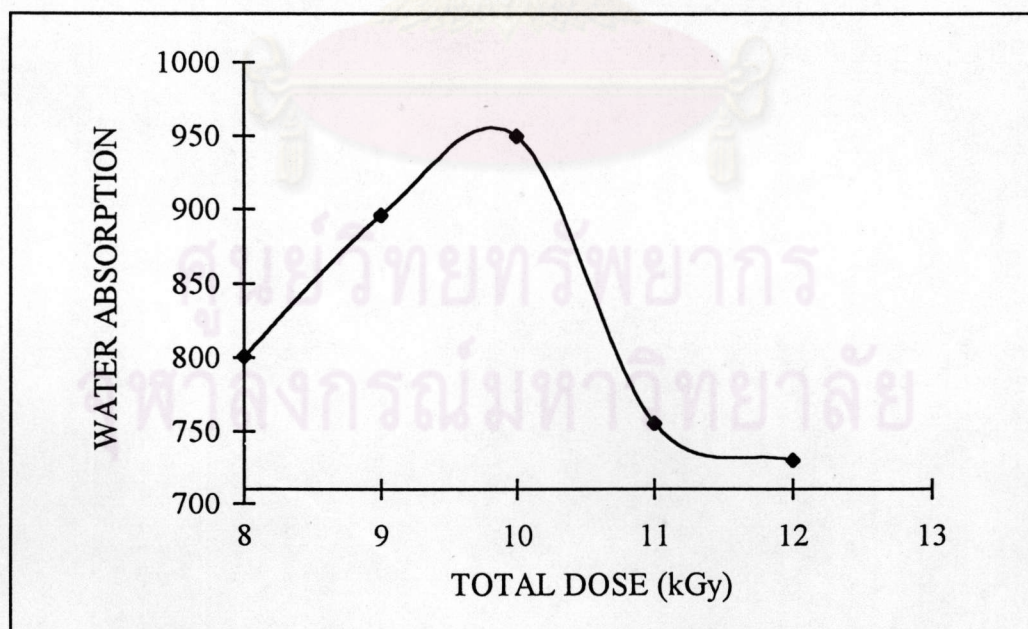


Figure 4.16 Effect of total dose(kGy) on water absorption(g/g).

Table 4.8 Effect of Dose Rate on Copolymerization of Partially Hydrolyzed Polyacrylamide(HPAM)-1-vinyl-2-pyrrolidone at the Total Dose of 10 kGy.

Dose Rate(kGy/min)	Conversion(%)	Water Absorption(g/g)
3.60×10^3	69	890
5.34×10^3	71	940
1.19×10^4	79	952

2.1 Relationship between Dose Rate and the Conversion of Monomer

The effect of the dose rate on the conversion of monomer is given in Table 4.8 and illustrated in Figure 4.17. When increasing the quantities of dose rate from 3.60×10^3 to 1.19×10^4 Gy/h, the conversion of monomer increases from 69 to 79%. The increasing trend of the conversion of monomer suggests that, in order to keep the total dose at a constant level, a low dose rate requires the longer irradiation time for the reaction to take place than that of a high dose rate to the same level of total dose. The lower dose rate produced a few radicals, and perhaps few cationic species in existence for the reactions. It does depend greatly on the magnitude of the half life of radicals. In the normal case, the radical half life could be as long as 3 - 4 days after an exposure to gamma rays, which should allow any post reaction of homopolymer formation and copolymerization to occur. But in this particular case, the reactions was stopped immediately after removing it from the source. Therefore, the effect of post irradiation can certainly be ignored. At the higher dose rates of gamma irradiation, several phenomena were observed elsewhere

(3). Due to that the abundant free radicals could initiate a large amount of growing chains of copolymer and homopolymer, the existing growing chains were then completely and rapidly scavenged by the monomer, and those growing chains were also not active by primary termination which involves propagating radicals reacting with primary radicals. The former reactions were the attribute to the high conversion of the system.

2.2 Relationship between Dose Rate and Water Absorption.

The effect of dose rate on water absorption in deionized distill water by partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) is tabulated in Table 4.8 and shown in Figure 4.18. The results show that the highest water absorption occurred at a dose rate of 1.19×10^4 Gy/h. The lower dose rate gives the lower absorption.

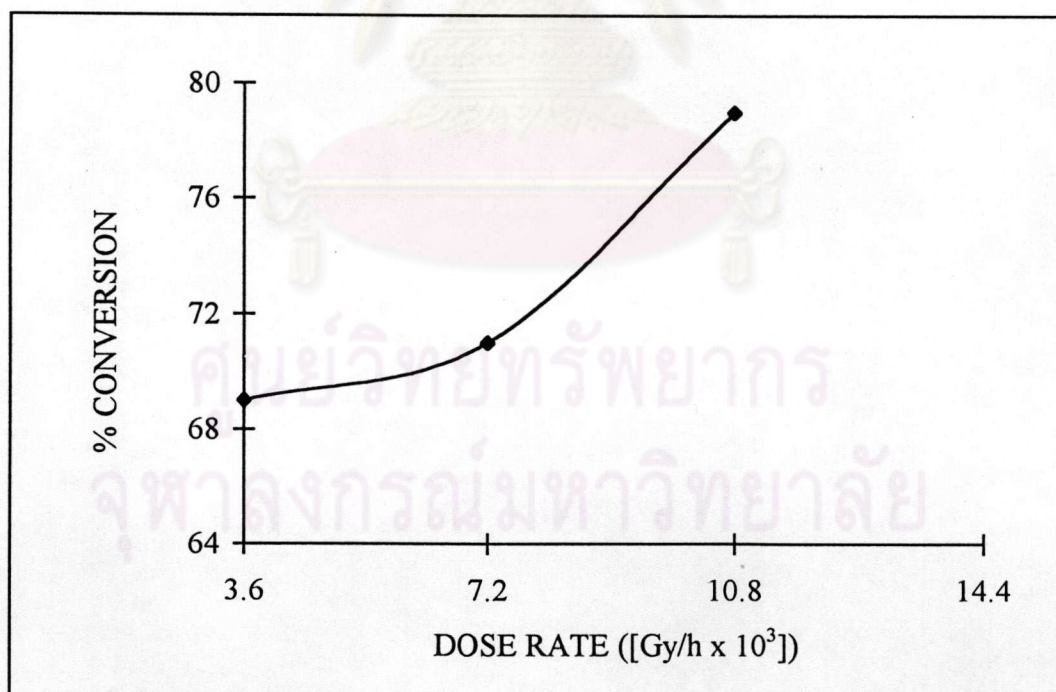


Figure 4.17 Effect of dose rate(Gy/h) on percentage conversion.

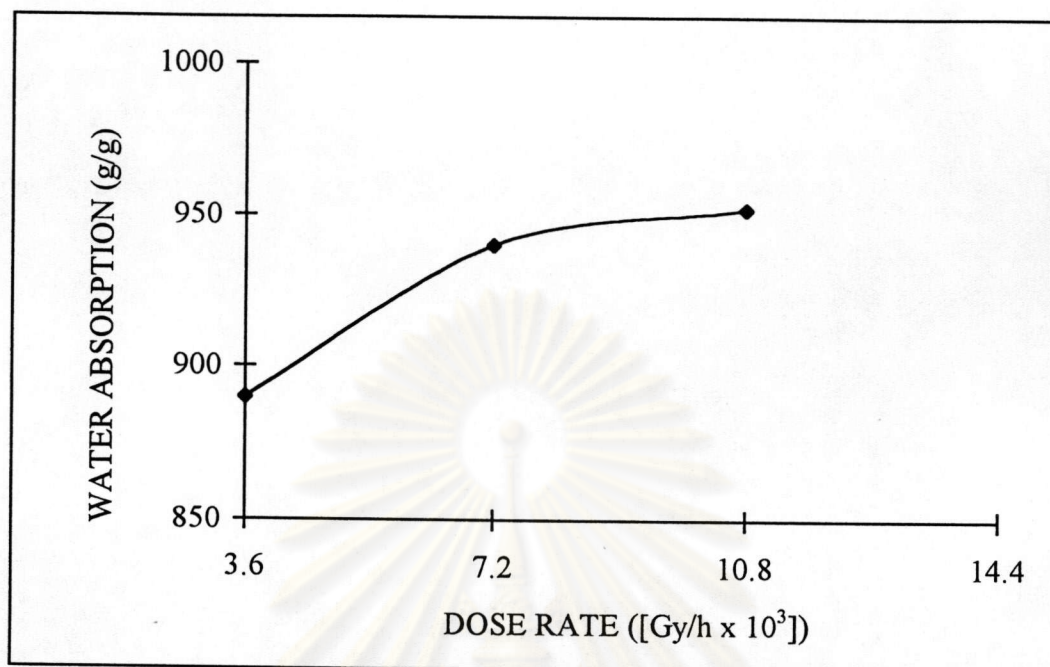


Figure 4.18 Effect of dose rate(Gy/h) on water absorption(g/g).

To conclude the effects of total dose and dose rate on copolymerization, one may possibly note that the extent of dose rate determines the length of branches whereas total dose controls the number of active sites for branching. The plausible explanation could be the difference in molecular weights of PVP and HPAM that affect the diffusions of the irradiated monomer, polymer and their growing chains.

3. Effect of the Amount of HPAM on Copolymerization.

The result of the effect of the amount of HPAM on copolymerization of partially hydrolyzed poly(acrylamide(HPAM)-co-1-vinyl-2-pyrrolidone) by gamma irradiation at a fixed dose rate of 1.19×10^4 Gy/h is presented in terms of the water absorption(g/g) as shown in Table 4.9 and Figure 4.19.

Table 4.9 Effect of the Amount of HPAM(g) incorporating in the Copolymer on Water Absorption.

HPAM(g)	Water absorption(g/g)
5	950
10	916
15	910
20	902

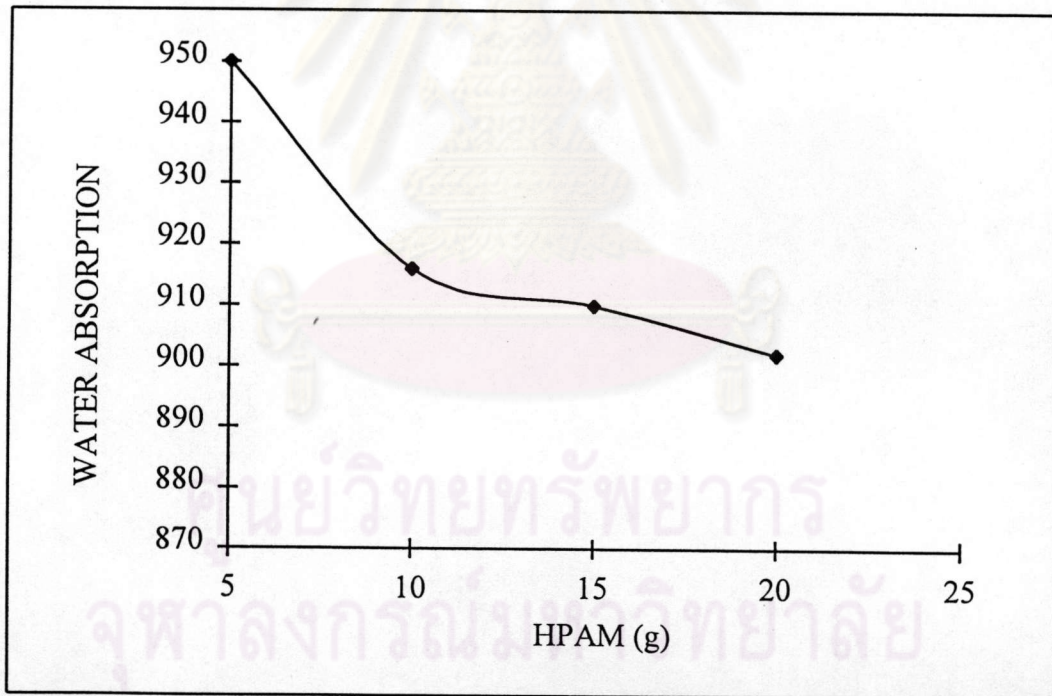


Figure 4.19 Effect of the amount of HPAM(g) incorporating in the copolymer on water absorption(g/g).

The results show that the highest water absorption occurred at the amount of HPAM(g) of 5 g. The higher quantity of HPAM gives the lower absorption. At the quantity of HPAM lower than 5 g copolymerization could not occur. It can be suggested that there a critical amount of HPAM required for copolymerization.

4. Effect of the Quantity of 1-Vinyl-2-Pyrrolidone on Copolymerization.

The result of the effect of the quantity of 1-Vinyl-2-pyrrolidone on copolymerization of partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) is presented in terms of water absorption(g/g) as tabulated in Table 4.10 and shown in Figure 4.20.

Table 4.10 Effect of the Quantity of 1-Vinyl-2-Pyrrolidone on Copolymerization.

Concentration of 1-vinyl-2-pyrrolidone(M*)	Water absorption in deionized distilled water(g/g)
0.47	884
0.94	950
1.41	638
1.88	637

* Calculated from 5, 10, 15 and 20 ml of the monomer.

The results show that the highest water absorption occurred at the quantity of 1-vinyl-2-pyrrolidone 0.94 M. The higher quantities of 1-vinyl-2-pyrrolidone give the lower water absorption; and likewise, the quantities of 1-vinyl-2-pyrrolidone lower than 0.94 M also give the lesser water absorption.

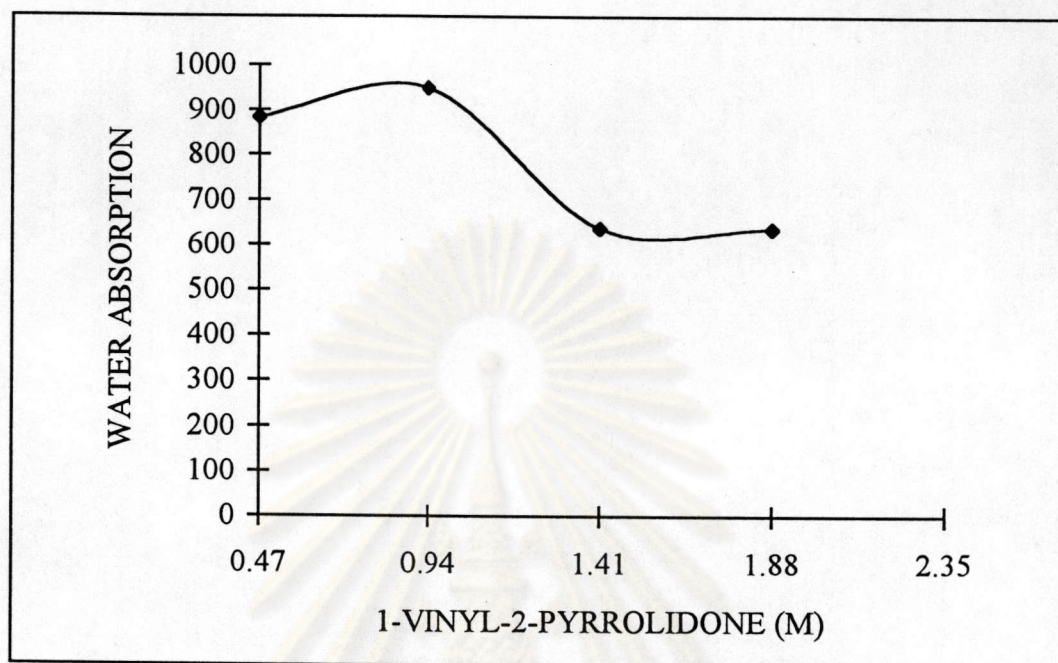


Figure 4.20 Effect of the quantity of 1-vinyl-2-pyrrolidone on water absorption.

5. Effect of the Degree of Hydrolysis of Polyacrylamide on Copolymerization.

The result of the degree of hydrolysis of polyacrylamide on copolymerization of partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) is presented in terms of water absorption shown in Table 4.11 and Figure 4.21.

Table 4.11 Effect of the Degree of Hydrolysis of Polyacrylamide on Copolymerization.

Degree of hydrolysis (%)	Water absorption in deionized distilled water(g/g)	
	HPAM	Copolymer
63	21	815
71	23	950
72	24	750
76	24	389
77	24	352
80	24	255
84	24	176

*Water absorption in deionized distilled water of PAM was 18 g/g.

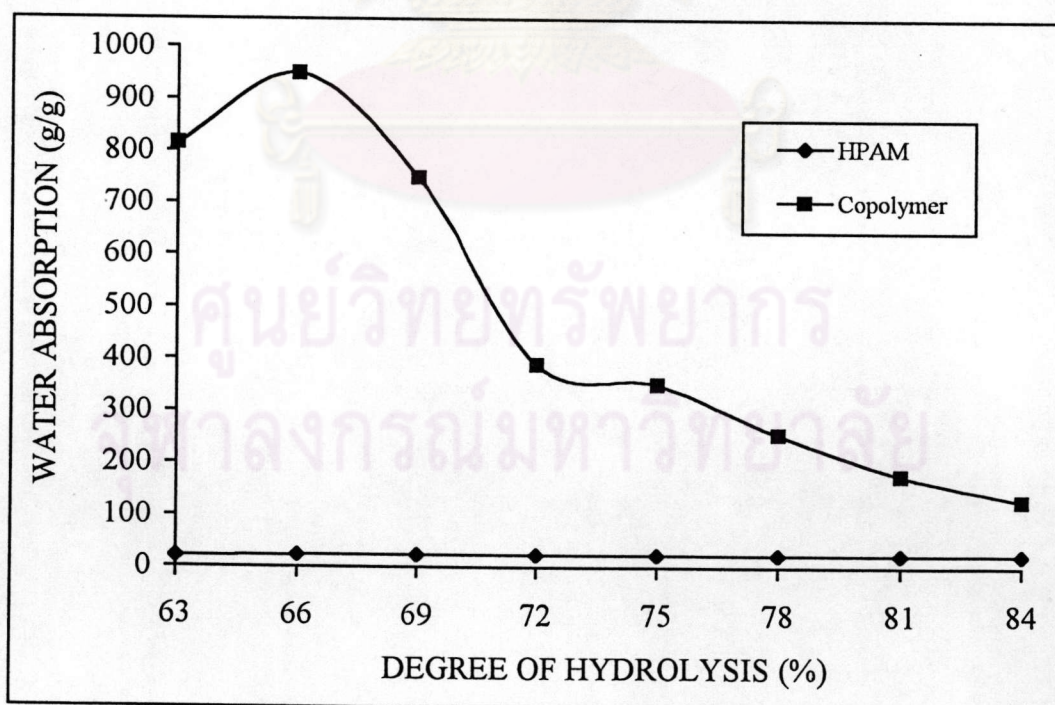


Figure 4.21 Effect of the degree of hydrolysis of polyacrylamide on copolymerization.

From Table 4.11 and Figure 4.21, the water absorption of the partially hydrolyzed polyacrylamide increased with increasing the degree of hydrolysis up to 71 %. After the degrees of hydrolysis higher than 71%, the water absorption are constant. The water absorption of partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) is highest at the degree of hydrolysis of 71%. The water absorption of the copolymer decreased with increasing degree of hydrolysis.

At low degrees of hydrolysis, the number of carboxyl groups is very low and randomly distributed(9): any hydrogen bonds formed will be unable to sustain a stable intramolecular complex. At low degrees of hydrolysis, the expansion of the HPAM coils is less than those at higher degrees. Therefore, at the low degrees of hydrolysis, it is not the dissociation of -COONa groups that prevent interactions with PVP. It can be suggested that there is a critical number of -COONa groups required for complexation with PVP. The interactions between the -COONa groups of the partially hydrolyzed polyacrylamide and the bulky functional groups of the PVP could cause steric hindrances, resulting in decreased mobility of the complex and a more rigid chain. The hydrogen bonding between the -COONa of the partially hydrolyzed polyacrylamide and PVP will be strong on account of the high electronegativity of the oxygen of PVP due to the presence of nitrogen(9).

Interactions are absent only when all the -COONa of HPAM are ionized. Interpolymer interactions between PVP and -COONa groups, which favored over the intrapolymer interactions between the amide and the acid groups. When the degree of hydrolysis is higher, there is no interaction between PAM and PVP. A possible explanation of this lies in the number of amide and acid groups present on the polymers. At low degrees of hydrolysis the number of amide groups is much higher than that of the acid groups. Interactions between the few widely scattered -COONa groups and the 1-vinyl-2-pyrrolidone groups will be weak. Poly(1-vinyl-2-pyrrolidone) will interact

with the amide groups, and this weak interaction results in only a slight decrease in the segmental mobility of HPAM. As the number of -COONa groups increases (higher percent hydrolysis and lower amide groups), interaction between the -COONa and poly(1-vinyl-2-pyrrolidone) will increase. Under these conditions, the number of amide groups is apparently too low for any significant interaction with poly(1-vinyl-2-pyrrolidone) and interactions between poly(1-vinyl-2-pyrrolidone) and the -COONa group dominate. The higher the degree of hydrolysis, the larger the number of hydrogen bonds and therefore the lesser the segmental mobility of the complex(9).

6. Water Absorption and Wicking Time of Partially Hydrolyzed Poly(acrylamide-co-1-vinyl-2-pyrrolidone: Dependence on Drying Method.

According to the results of the dose rate of 1.19×10^4 Gy/h and total dose of 10 kGy, the copolymer of the partially hydrolyzed poly (acrylamide-co-1-vinyl-2-pyrrolidone) have the maximum water absorption in deionized distilled water, of 950 times its dried weight.

Table 4.12 The Water Absorption and Wicking Time of Partially Hydrolyzed Poly(acrylamide-co-1-vinyl-2-pyrrolidone): Depended on the Drying Method.

Degree of Hydrolysis(%)	Water Absorption(g/g)		Wicking Time(min)	
	Heat Dried	Freeze Dried	Heat Dried	Freeze Dried
63	815	965	16.10	17.25
71	950	1100	24.45	25.30
72	750	897	12.45	14.20
76	389	539	9.30	10.30
77	352	502	7.55	8.25
80	255	406	6.30	7.10
84	176	328	3.00	3.50

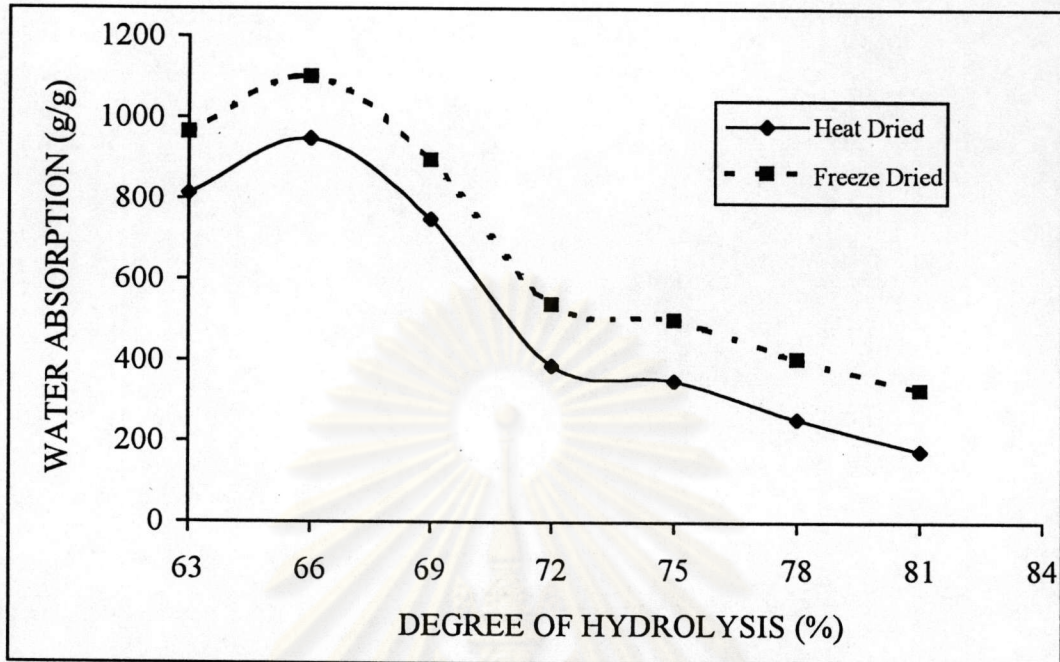


Figure 4.22 Water absorption of partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) with the different drying methods.

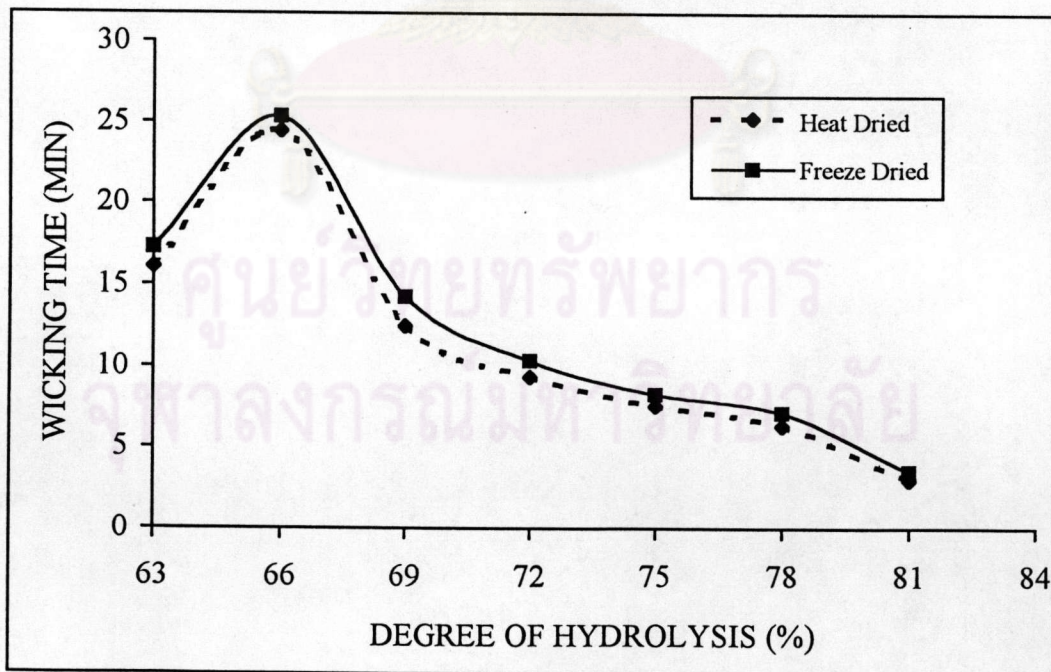


Figure 4.23 Wicking time of partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) with the different drying methods.

In Table 4.12, Figures 4.22 to 4.23 the water absorption and wicking time of the absorbent copolymer are shown. Drying methods imposes a strong influence on water absorption. Heat drying method gives the product with less water absorption than does freeze drying method because there are reactive side groups along the copolymer chain (-COONa or -CONH₂), that side branching and crosslinking of copolymer can occur to stiff the chains under during drying leading to a declineing water absorpency.

7. 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 % NaCl w/v on the water absorption is clearly illustrated in Table 4.13 and Figure 4.24. The water absorption efficiency of the copolymer is very dependent on the ion concentration. Indeed, the effect of NaCl at different concentrations show a dramatic decrease in water absorption of the copolymer.

Table 4.13 Effect of NaCl Concentration on Water Absorption.

Concentration of NaCl(% w/v)	Water Absorption in g/g
0	950
0.1 ^a	310
0.5 ^b	205
1.0 ^c	130
2.0 ^d	96

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

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

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

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

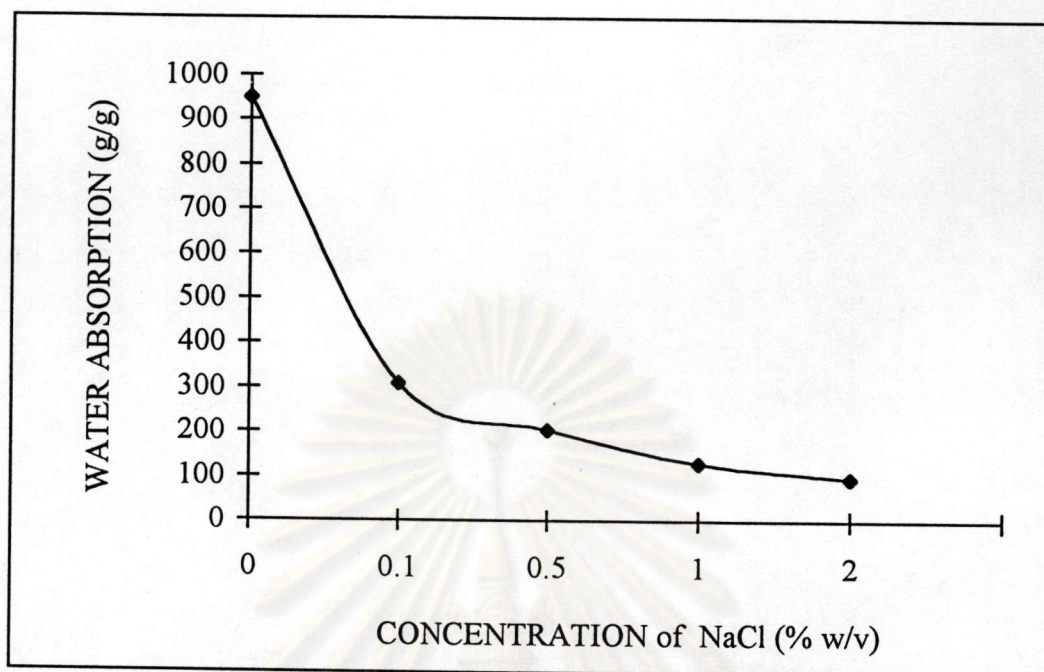


Figure 4.24 Effect of NaCl concentration on water absorption.

The ions attached to the macromolecule network in the gel are immobile and are considered to be separated from the external solution by a semipermeable membrane, which confines to 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(36).

In this case the copolymer is present at the anion of sodium salt (polycarboxylate) and polycarboxamide, which are assumed to be a strong electrolyte.

When copolymer was placed in NaCl solutions, at the surface of this material the behavior as semipermeable membrane exists. To maintain electrical neutrality on the both sides 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. 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 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 Na^+ ions in the interior of the gel have the same concentration (mole-ion/l) as that of polycarboxylate.

Then

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

- π : osmotic pressure, atm
 a: concentration of polycarboxylate and Na^+ 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, $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$.
 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 producing wells environment, a similar effect is expected as producing wells contain various types of ions. The use of partially hydrolyzed polyacrylamide(HPAM) copolymer in producing wells also has such an effect, a reduction in water absorption. HPAM is a polyelectrolyte, and as such it will interact quite strongly with ions in solution.

However, since the polyacrylamide chain is flexible, it may respond much more to the ionic strength of the aqueous solvent, and its solution properties are much more sensitive to salt than HPAM. In order to compensate for the decrease in water intake, the use of partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) is therefore necessary.

8. Effect of MgCl₂ Solutions on Water Absorption.

The water absorption of the partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) in 0.1, 0.5, 1.0 and 2.0 % w/v of magnesium chloride solutions is given in Table 4.14 and Figure 4.25.

Table 4.14 Effect of MgCl₂ Concentration on Water Absorption.

Concentration of MgCl ₂ (%W/V)	Water Absorption in g/g
0	950
0.1 ^a	153
0.5 ^b	96
1.0 ^c	63
2.0 ^d	43

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

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

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

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

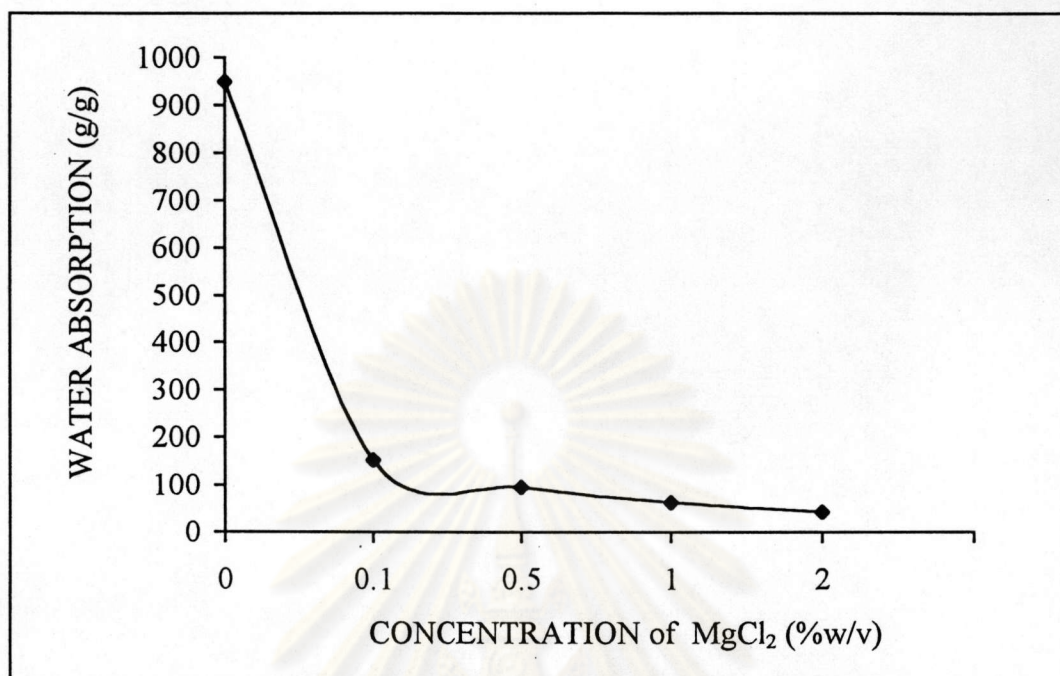



Figure 4.25 Effect of MgCl₂ concentration on water absorption.

On observing the case of MgCl₂, the water absorption decreased even more with increasing magnesium chloride concentrations. As a consequence, the absorption with MgCl₂ solution is much less than dose NaCl. Here the highest water intake of MgCl₂ solution is 153 g/g, while that of NaCl the value obtained is 310 g/g.

As the concentration of 0.1 % w/v of NaCl and MgCl₂, both Na⁺ and Mg²⁺ have ion concentrations of 0.034 and 0.030 mole-ion/l, respectively. The results 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 ions types. The water intake by the gel reduced the osmotic pressure until an ion concentration equilibrium was reached.

9. Thermal Properties of Polyacrylamide, Poly(1-Vinyl-2-Pyrrolidone) and Copolymers at Various Degrees of Hydrolysis of Partially Hydrolyzed Polyacrylamide.

The thermal properties of polyacrylamide, poly(1-vinyl-2-pyrrolidone) and copolymers at various degrees of hydrolysis of partially hydrolyzed polyacrylamide were studied by thermogravimetric analysis(TGA) in the range 50 - 650°C under nitrogen atmosphere and heating rates 20°C/min. The decomposition temperatures of polyacrylamide, poly(1-vinyl-2-pyrrolidone) and copolymers at various degrees of hydrolysis of partially hydrolyzed polyacrylamide are shown in Table 4.15 and Figures 4.26 - 4.32.



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Table 4.15 The Decomposition Temperatures of Polyacrylamide, Partially Hydrolyzed Polyacrylamide at Various Degree of Hydrolysis, Poly(1-Vinyl-2-Pyrrolidone) and Copolymers at Various Degrees of Hydrolysis of Partially Hydrolyzed Polyacrylamide.

Sample	Decomposition Temperature(°C)
PAM	424.17
63% HPAM	390.50
71% HPAM	394.80
76% HPAM	388.00
80% HPAM	386.50
84% HPAM	385.00
PVP	456.19
63% HPAM-co-PVP	440.97
71% HPAM-co-PVP	446.53
76% HPAM-co-PVP	443.38
80% HPAM-co-PVP	440.07
84% HPAM-co-PVP	436.42

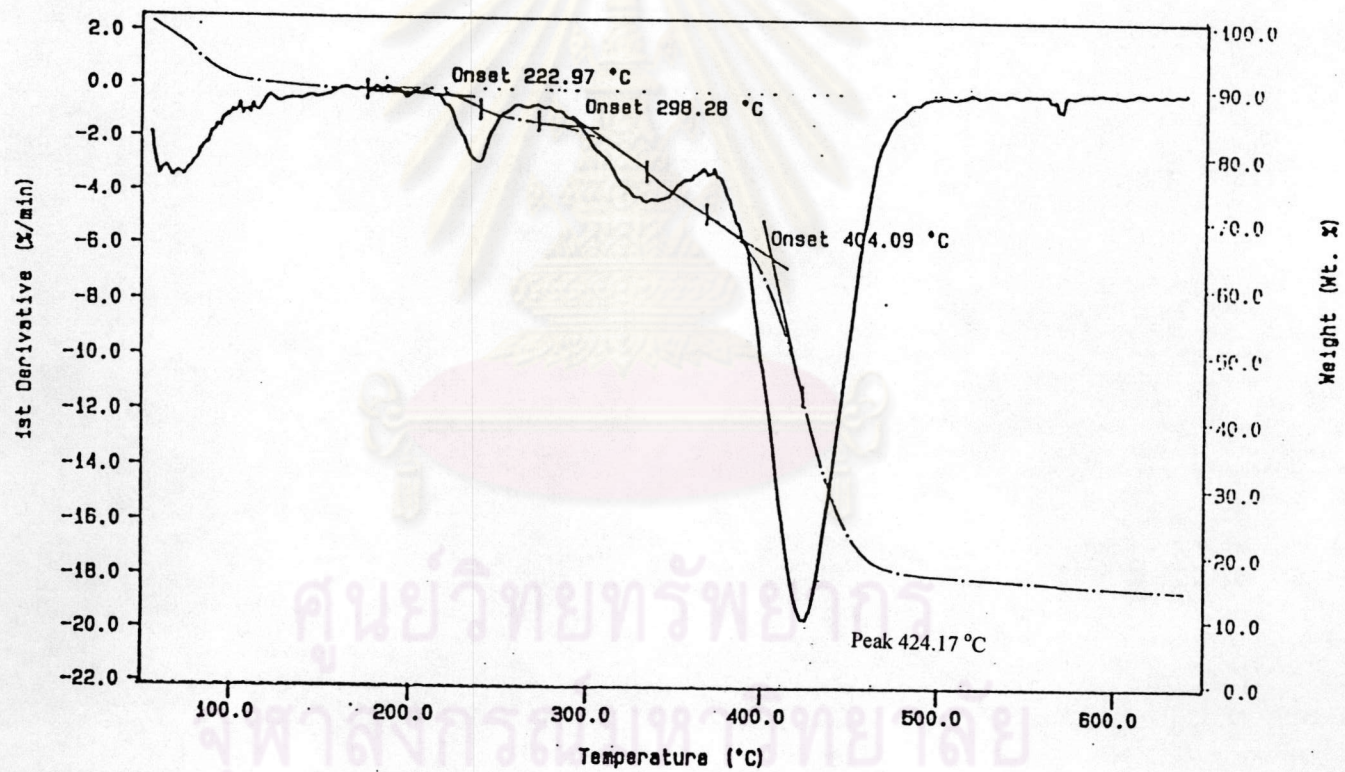


Figure 4.26 Thermogravimetric curve of PAM

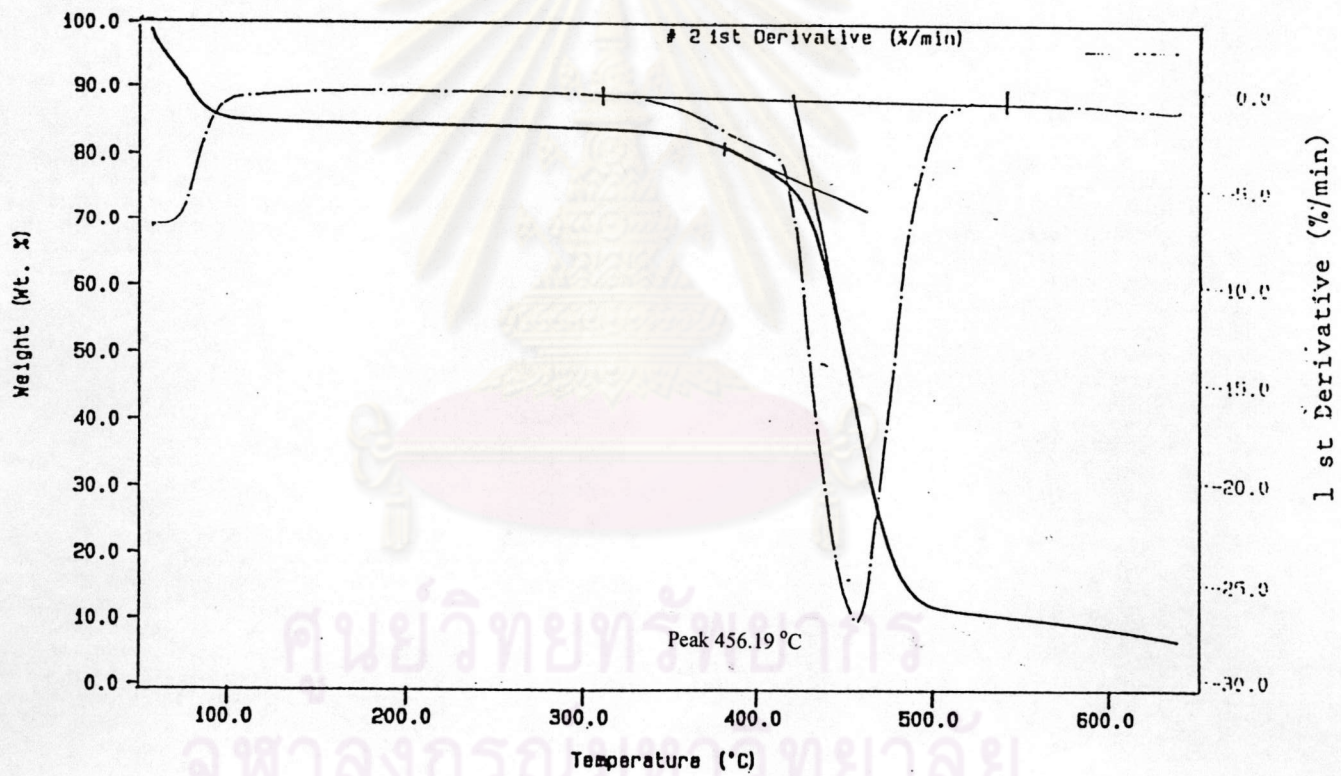


Figure 4.27 Thermogravimetric curve of PVP

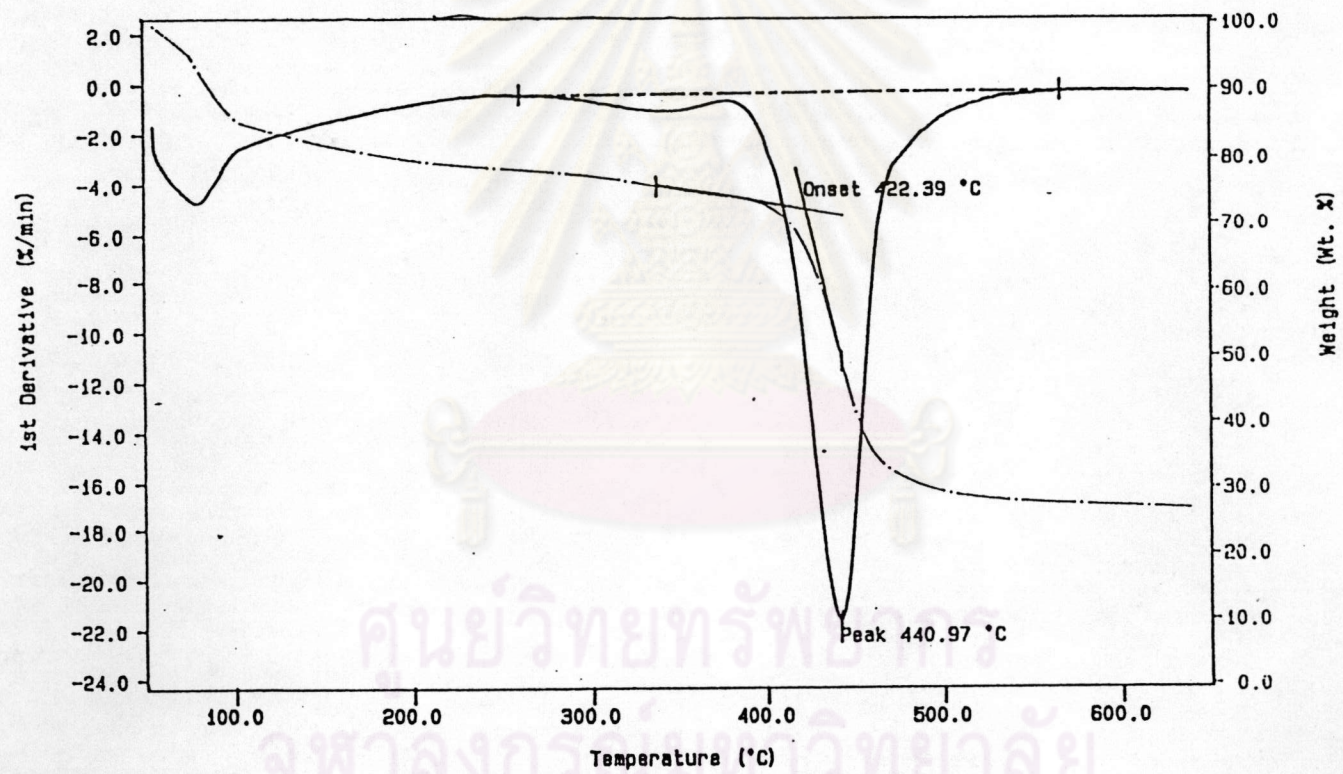


Figure 4.28 Thermogravimetric curve of 63% HPAM-co-PVP

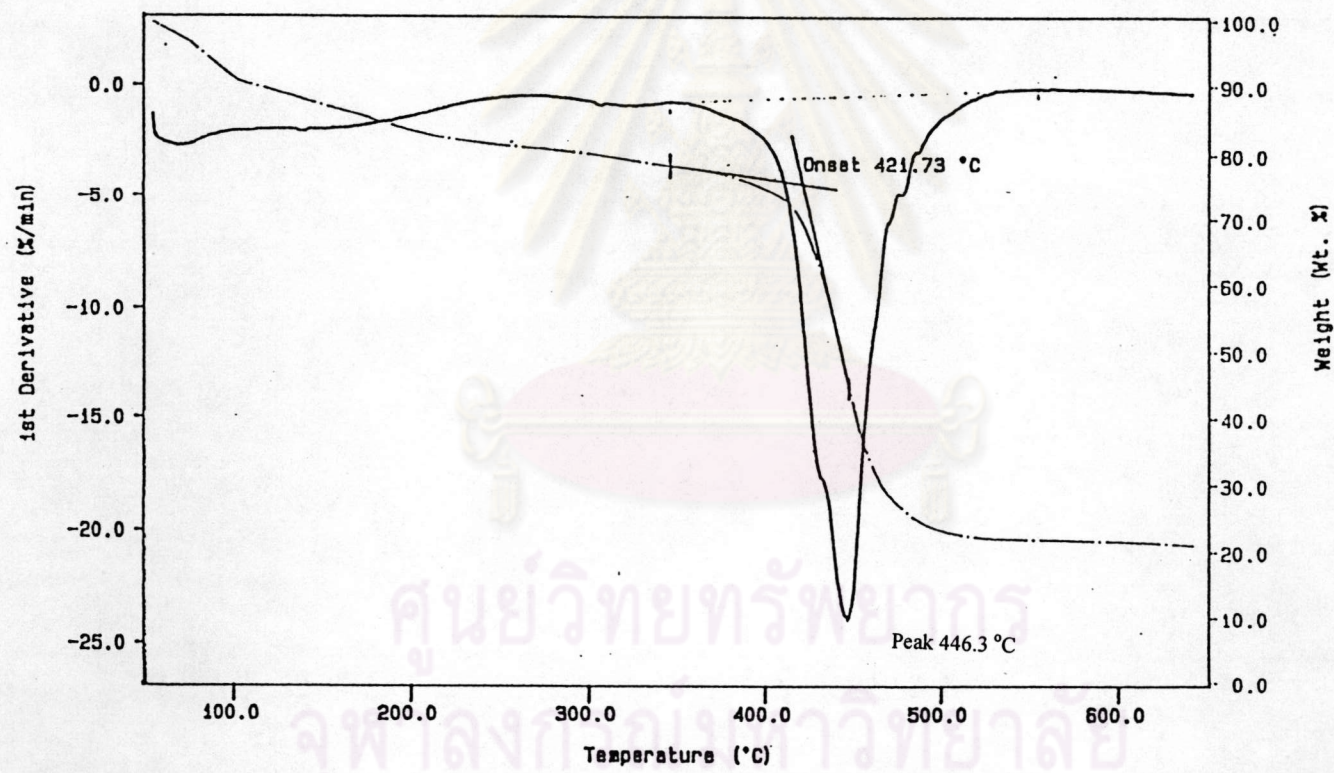


Figure 4.29 Thermogravimetric curve of 71% HPAM-co-PVP

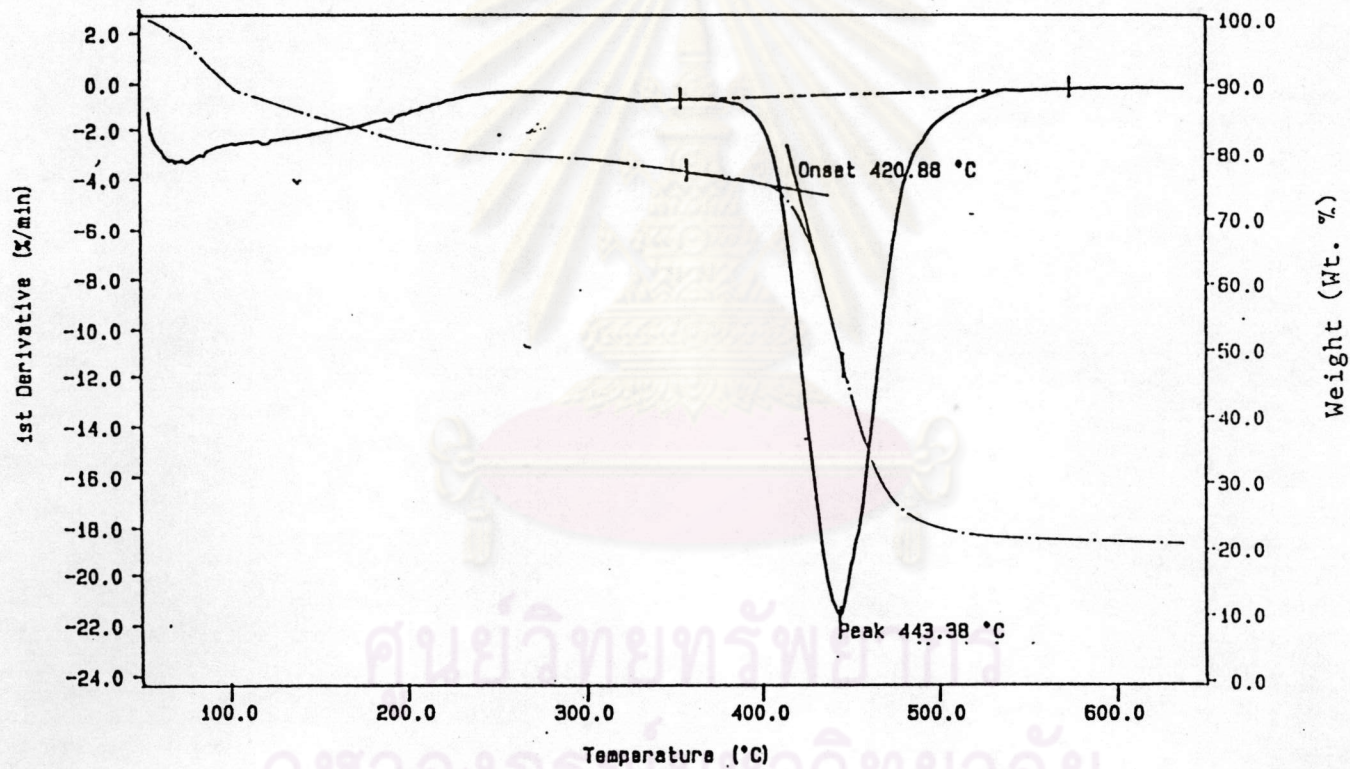


Figure 4.30 Thermogravimetric curve of 76% HPAM-co-PVP

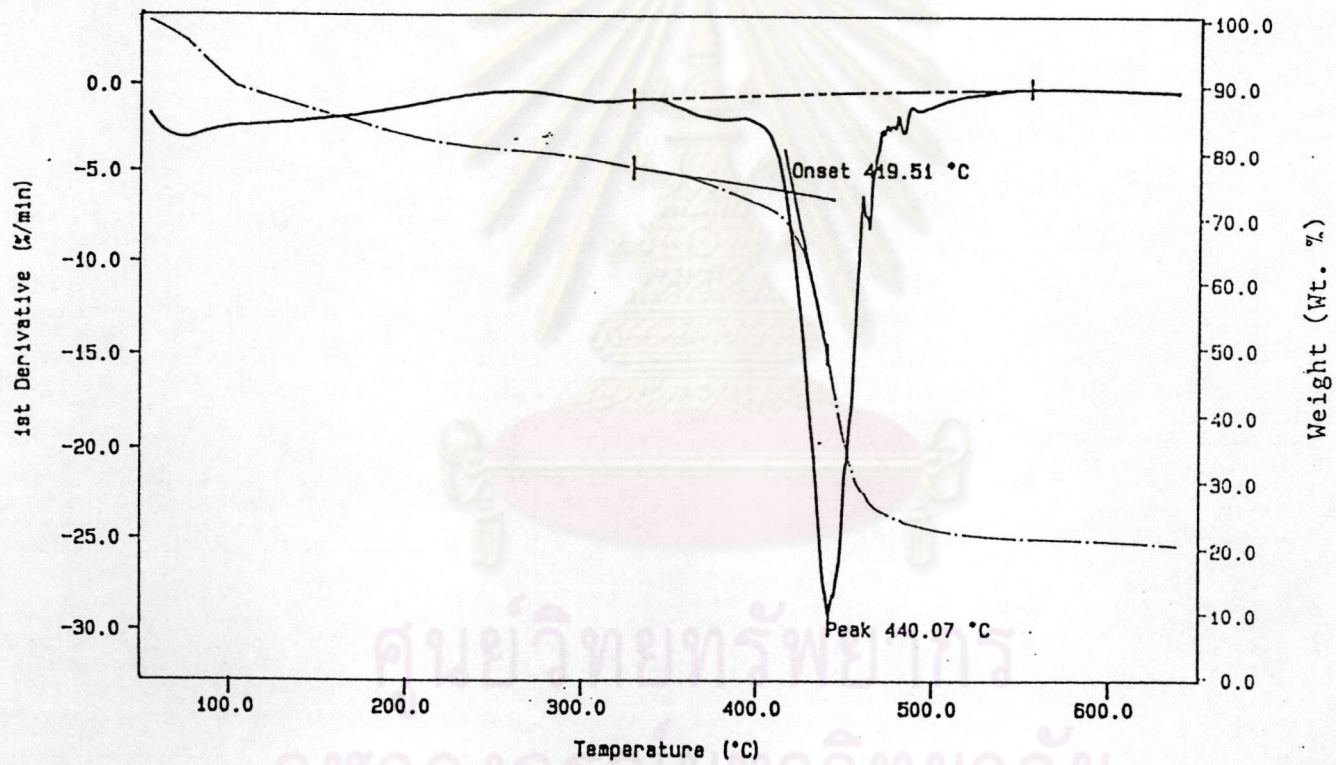


Figure 4.31 Thermogravimetric curve of 80% HPAM-co-PVP

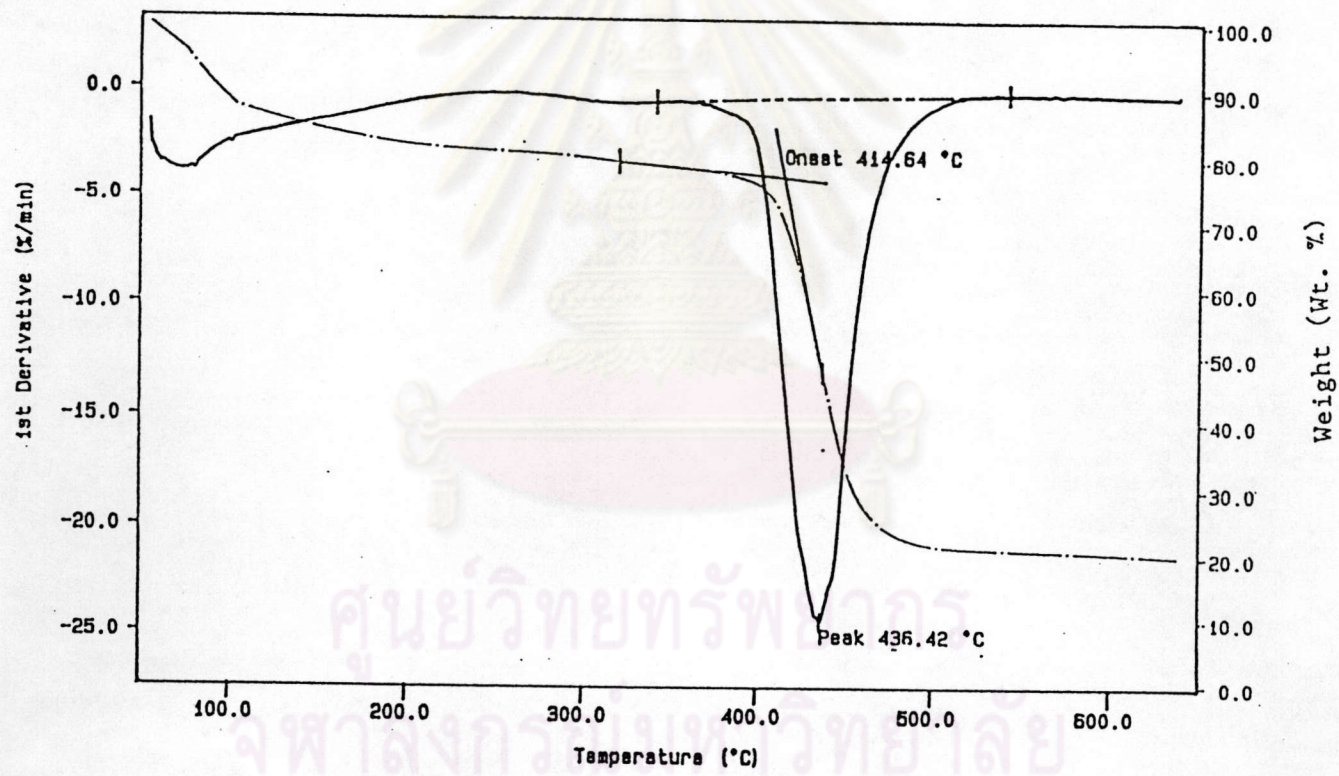


Figure 4.32 Thermogravimetric curve of 84% HPAM-co-PVP

Figures 4.26 - 4.32 show TGA curves for the decomposition temperatures of polyacrylamide, poly(1-vinyl-2-pyrrolidone) and copolymers at various degrees of hydrolysis of partially hydrolyzed polyacrylamide. The highest decomposition temperature of copolymer occurred at the degree of hydrolysis of partially hydrolyzed polyacrylamide of 71%. The higher degree of hydrolysis other than 71% HPAM-co-PVP gives the lower decomposition temperatures. The results of TGA analyses show that copolymers have significantly higher thermal stability than PAM (about 20°C higher). This is likely due to the presence of poly(1-vinyl-2-pyrrolidone). According to the bond energy, the C-N linkage (292 kJ/mol) is weaker than the C-C (348 kJ/mol), C-O (351 kJ/mol), or C-H (391 kJ/mol). Therefore, it can be reasonably expected that the thermal degradation proceeds through the breaking of the C-N bond better than the random scission of the C-C main chain. This behavior could justify the release of pyrrolidone as the main product of the initial step of the degradative pathway. These facts support a degradative mechanism through the release of the pyrrolidone side group represented in Figure 4.32.

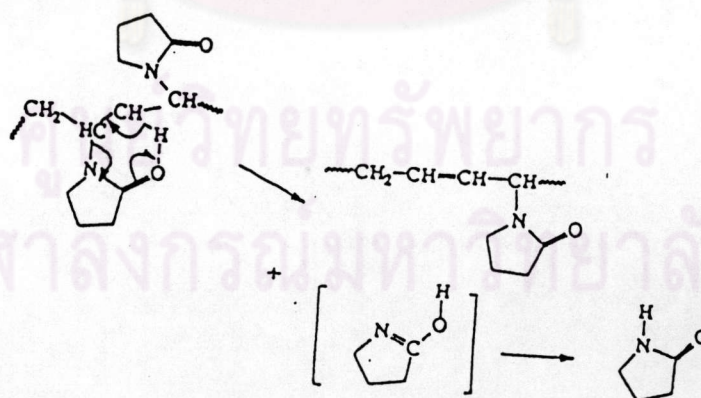


Figure 4.33 Degradative mechanism of poly(vinyl pyrrolidone)