CHAPTER IV

RESULTS and DISCUSSION

4.1 The Optimum Concentration of the Monomer Solution

The result of the first set of water absorbency test of the copolymer beads synthesized by inverse suspension polymerization with various concentrations of the monomer solutions was in Table 4.1.
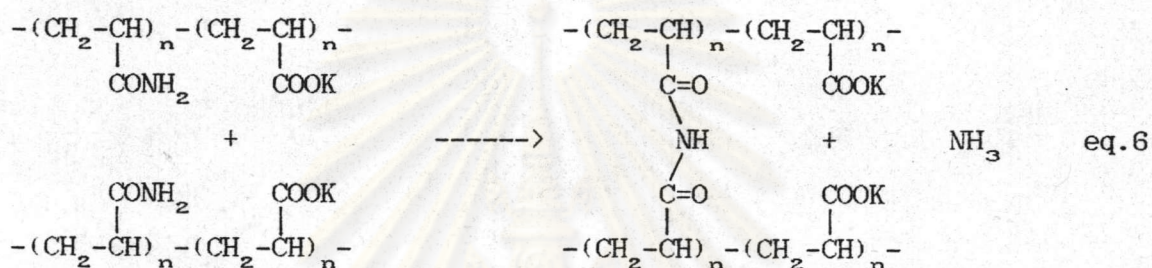
TABLE 4.1

Effect of the Monomer Concentration

on the Water Absorbency of the Synthesized Copolymers

Molar ratio of Am : KA	Water Absorbency (g H_2O / g dry polymer)
10 : 90	Soluble
30 : 70	Soluble
50 : 50	Soluble
70 : 30	Soluble
71 : 29	347
72 : 28	Soluble
90 : 10	Soluble

The synthesized copolymers of Am and KA are soluble in water on account of the hydrophilic pendants (amide and carboxylate groups) in their structure, except that the molar ratio of Am:KA at 71:29 produced the water insoluble beads with high-water absorbency values of 347 times its dry weight. It is speculated that gel formation in

the absence of crosslinking monomer is probably due to the following side reactions:

a. the occurrence of imidization that usually takes place in the polymerization of acrylamide in concentrated solutions (27) and at high temperature(12,27). The imidization of the amide pendents in the copolymer is shown below:

$$-(CH_2-CH)_n-(CH_2-CH)_n- \qquad\qquad -(CH_2-CH)_n-(CH_2-CH)_n-$$
$$\qquad | \qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad | \qquad\qquad\qquad | $$
$$\qquad CONH_2 \qquad\quad COOK \qquad\qquad\qquad\qquad C=O \qquad\quad COOK$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \backslash$$
$$\qquad + \qquad\qquad ------> \qquad\qquad NH \qquad + \qquad NH_3 \qquad eq.6$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad /$$
$$\qquad CONH_2 \qquad\quad COOK \qquad\qquad\qquad\qquad C=O \qquad\quad COOK$$
$$\qquad | \qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad | \qquad\qquad\qquad | $$
$$-(CH_2-CH)_n-(CH_2-CH)_n- \qquad\qquad -(CH_2-CH)_n-(CH_2-CH)_n-$$

b. polymerizing highly concentrated solutions of acrylic acid, may cause an auto-crosslinking through a hydrogen abstraction from the polymer backbone followed by radical combinations (28). In addition, Takatsuki, M.M., and Meano, J. discovered that when acrylic acid salt is polymerized with the water-soluble persulfate, crosslinking proceeds without using a crosslink agent (29).

c. chain transfer to polymer may occur during the polymerization.

The critical molar ratio of Am:KA at 71:29 produced the best HWAP, indicates that one of the side reactions should be crosslinking of the copolymer with an appropriate crosslink density. The structure of the copolymer should consist of more acrylate units than the acrylamide units owing to the higher hydrophilicity of the carboxylate group, and the reactivity ratio of KA is higher than that of Am. The copolymerization reactivity ratios of KA and Am are 1.35 and 0.78, respectively(30).

4.2 The Optimum Polymerization Temperature

The water absorbency of the copolymer beads synthesized at 71:29 molar ratio of Am:KA with 1.4 g/l $(NH_4)_2S_2O_8$ at various polymerization temperatures between 40-60 °C was shown in Table 4.2.

TABLE 4.2

Effect of the Polymerization Temperature

on the Water Absorbency of Synthetic Beads

Polymerization Temperature (°C)	Water Absorbency (g H_2O / g dry polymer)
40	Soluble
45	Soluble
50	66
60	347

At low temperatures (40 and 45 °C), the synthetic copolymers are water soluble; but at higher temperatures, the polymerization provided crosslinked copolymers having water absorbency values of 66 and 347 g/g at 50 and 60 °C, respectively. The results support that self-crosslink should occur at higher temperatures to give insoluble products.

4.3 The Optimum Concentration of the Initiator

The results of inverse suspension copolymerization of Am:KA synthesized with various concentrations of $(NH_4)_2S_2O_8$ were shown in Table 4.3 and Figure 4.1.

TABLE 4.3

Effect of the Initiator Concentration
on the Water Absorbency of Synthetic Beads

$[(NH_4)_2S_2O_8]$ (g/l)	Water Absorbency (g H_2O / g dry polymer)
0.5 (2.19×10^{-3})	43
1.0 (4.39×10^{-3})	31
1.4 (6.57×10^{-3})	347
1.6 (8.76×10^{-3})	124
2.0 (10.95×10^{-3})	53

The values in the parenthesis indicate the initiator concentrations in mol/dm^3 unit.

The optimum initiator concentration was 1.4 g/l to give the copolymer which has the highest water absorbency.

4.4 The Optimum Quantity of the Crosslinking Agent

The water absorbency of the crosslinked copolymers synthesized with 71:29 molar ratio of Am:KA and at $60°C$ with 1.4 g/l $(NH_4)_2S_2O_8$ at various concentrations of N,N´-MBA was shown in Table 4.4 and Figure 4.2.
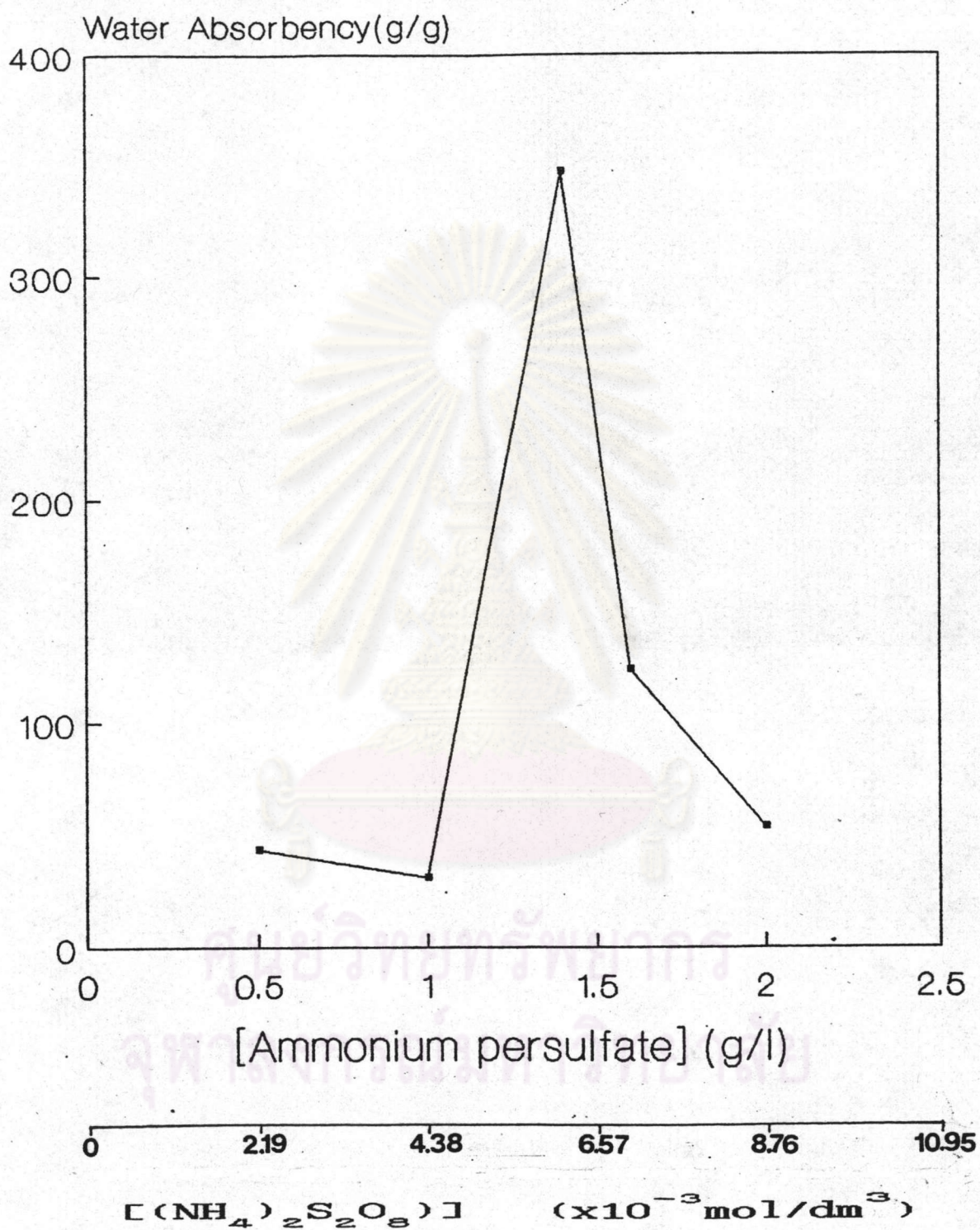
FIGURE 4.1 Effect of the initiator concentration on
the water absorbency of synthetic beads

TABLE 4.4

Effect of the Crosslinking Agent Concentration

on the Water Absorbency of Synthetic Beads

[N,N´-MBA] (mole%)	Water Absorbency (g H_2O / g dry polymer)
0	347
0.005	38
0.010	25
0.020	43
0.030	45
0.040	122
0.050	47

The copolymer crosslinked with N,N´-MBA gave the best product at 0.40 mole% N,N´-MBA with a water absorbency of 122 g/g, but the extent of water absorption is lower than that of the best water-absorbing copolymer synthesized in the absence of crosslink. This was ascribed to the formation of more crosslinks which inhibit the swelling of the gel. In general, crosslinking agents have been employed to help improve the rate of fluid absorption. However, if the degree of crosslinking is too high, the absorbency will be decreased. The absorbency of crosslinked polymers can be explained in terms of swelling. Swelling is a diffusion phenomenon driven by the affinity of the molecules of the swelling material for the molecules of the contracting fluid. A classical crosslinked network has a swelling limit controlled by a balance between the thermodynamic forces due to polymer-solvent interactions and the entropic force of coiled polymer chains.
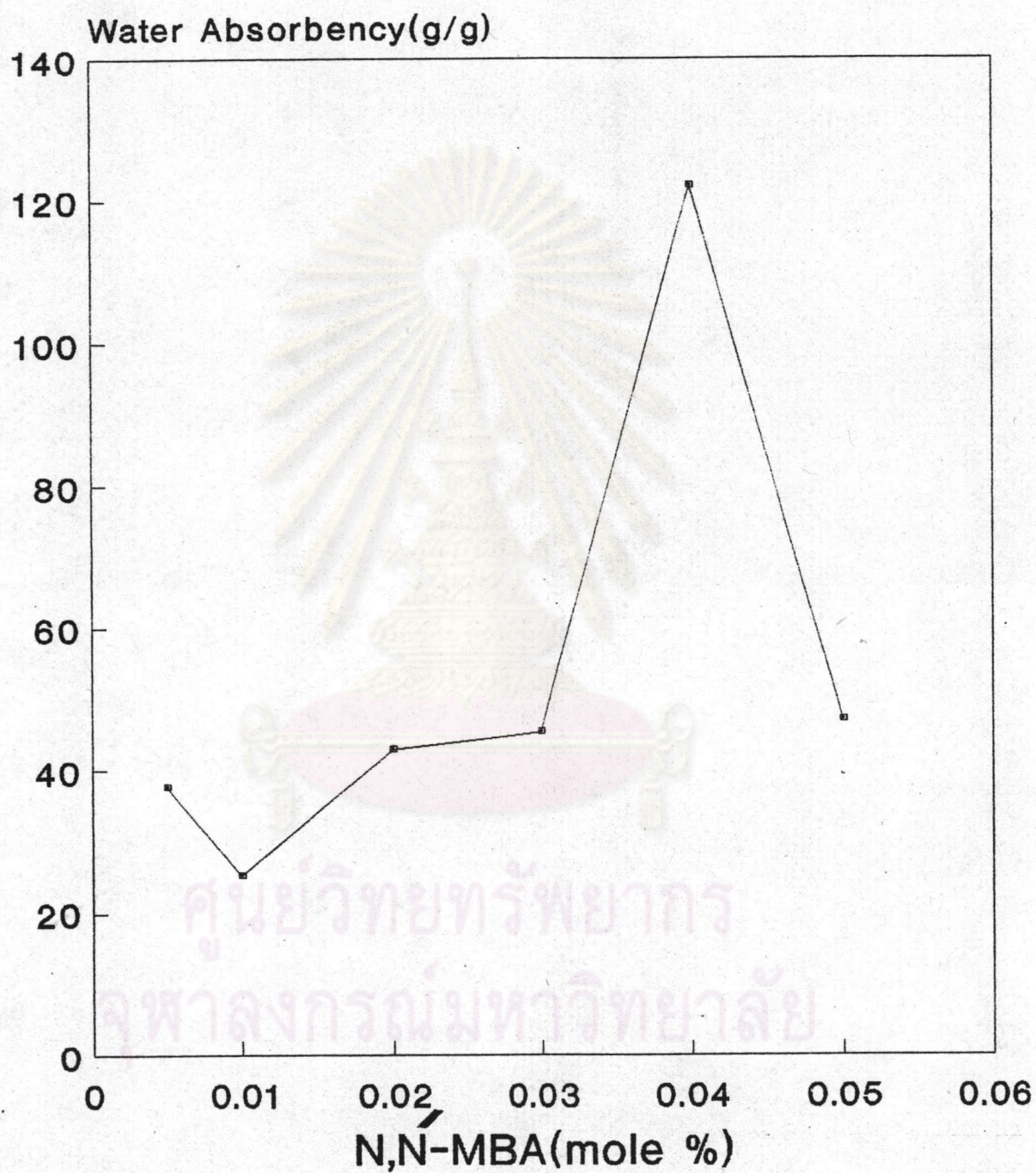
FIGURE 4.2 Effect of the crosslinking agent concentration
on the water absorbency of synthetic beads

A three-dimensional network of polymer in contact with a solvent will strive to dissolve in the liquid. In the process the polymer chains uncoil to more open conformations so that each chain can maximize its contact with the solvent molecules, and thus swelling of the network takes place. If there is no crosslink, the swelling would continue until a viscous solution is obtained. But in a crosslinked network as the chains between crosslinks become increasingly elongated, an elastic retractive force develops. The swelling will stop at an equilibrium point when the swelling force is balanced by the retractive force.

The swelling equilibrium is dependent on the entropy of dilution, the heat of dilution, and the entropy of the polymer network. For a given polymer-solvent system the equilibrium swelling is a function of the crosslink density. The relationship involving the equilibrium swelling ratio w, defined as the ratio of the final swollen volume to the original unswollen volume of the network, was derived by Flory (therein 31). If the crosslink density is not too high and the solvent is a good solvent, the following approximated relationship was obtained;

$$w^{5/3} = CM_c/(1-2M_c/M) \qquad \text{eq.7}$$

where $C = (0.5-u)/\rho_p v_s$ is a constant for a given polymer-solvent system, u is a dimensionless parameter expressing first neighbor interaction for solvent with polymer, ρ_p is the polymer density, v_s is the molar volume of the solvent, M_c is the average molecular weight per crosslink, and M is the average weight of the analogous uncrosslinked polymer.

In the case of a polyelectrolyte network, the swelling forces are increased by the ionic repulsion of like charges of the polymer chains. This further expands the network and increases the equilibrium

swelling(31). The swelling properties of a polymer are dependent upon the polymer character, crosslink density, and the ionic content. Crosslink density can be determined either by mechanical means or by equilibrium swelling measuerments which are appropriate for polymer samples of well defined geometry and water absorbing polymers synthesized by suspension polymerization as small, irregular particles or beads, repectively(28).

4.5 The Synthesis of Crosslinked Poly(acrylamide-*co*-potassium acrylate) by the Redox Initiator

The concentration ratio of $(NH_4)_2S_2O_8$:TMEDA of 2:1 by weight was used as a redox initiating system at $45\,^{\circ}C$ as the reaction temperature in the presence of N,N´-MBA. The water absorbency of the crosslinked copolymers at various N,N´-MBA .concentrations was tabulated in Table 4.5 and compared with the result of Section 4.4 by graphs in Figure 4.3.

Figure 4.3 shows that crosslinked copolymers synthesized by redox initiation with 0.020 and 0.050 mole% of N,N´-MBA have about twice water absorbency, higher than those synthesized by thermal initiation, but at 0.040 mole% of N,N´-MBA, thermal initiation produced a better crosslinked copolymer having the highest water absorbency of 122 g/g. Thus the appropriate concentrations of N,N´-MBA to crosslink the copolymer by thermal and redox initiation are 0.040 mole% and 0.020 or 0.050 mole%, respectively.

The inverse suspension polymerization occurred at lower temperature($45\,^{\circ}C$) than the polymerization with thermal initiator($60\,^{\circ}C$) is assinged in the patent literature(32) that a combination of thermal initiator with a reducing agent enables an efficient polymerization

while limiting the free monomer (acrylic acid and acrylic acid salt) content to less than 1,000 ppm, and generally less than 500 ppm in the completed water-absorbing polymer. However, the results show that the extent of water absorption of the crosslinked copolymers synthesized with redox initiator is much lower than that of the best HWAP produced by thermal initiation without a crosslinker possibly due to the more crosslinks in the copolymers.

TABLE 4.5

The water absorbency of the copolymer bead synthesized
with the redox initiating system

[N,N´-MBA] (mole%)	Water Absorbency (g H_2O / g dry polymer)
0.010	32
0.020	84
0.030	19
0.040	68
0.050	86

Many oxidation-reduction reactions produce radicals that can be used to initiate polymerization. A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0-50 °C and even lower. This allows a greater freedom of choice of the polymerization temperature than is possible with the thermal homolysis of initiation(4). The rate of polymerization in terms of the concentration of monomers and initiators, for bimolecular termination
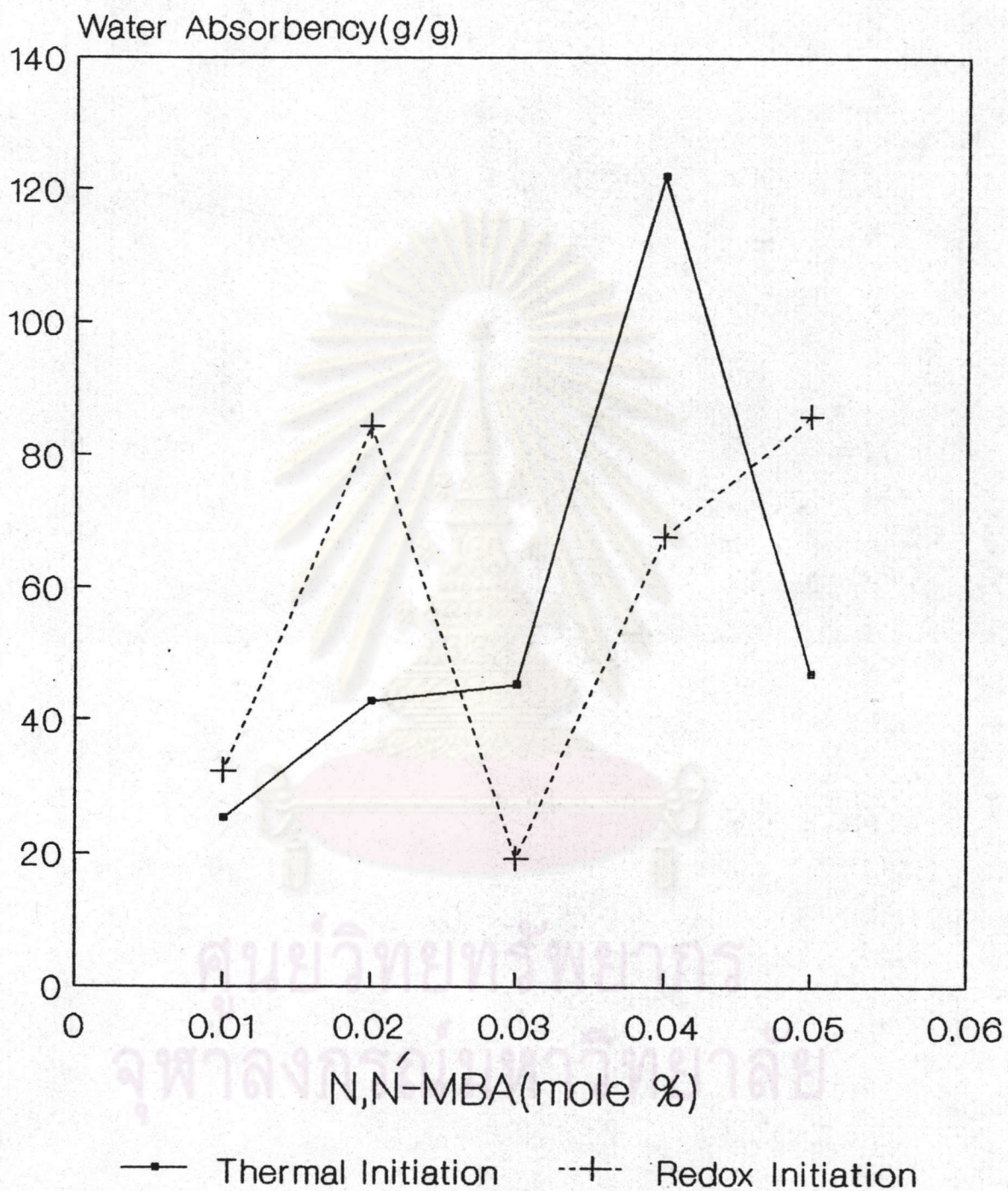
FIGURE 4.3 Comparison of water absorbency of the copolymers
synthesized by thermal and redox initiating system

is shown below:

for polymerization with thermal initiators

$$R_p = k_p[M]\{fk_d[I]/k_t\}^{1/2} \qquad \text{eq.8}$$

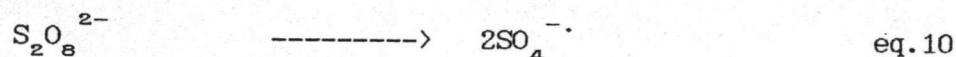for polymerization with redox initiators

$$R_p = k_p[M]\{fk_d[oxidant][reductant]/2k_t\}^{1/2} \qquad \text{eq.9}$$

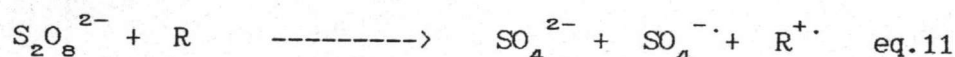R_p is the polymerization rate, k_p is the rate constant for the propagation step, k_d is the rate constant for initiator decomposition, k_t is the rate constant for the termination step, [M] is monomer concentration, f is an efficiency factor for the initiators, and [I], [oxidant], and [reductant] are concentrations of the initiators. The general first-order dependence of rate on monomer concentration is altered when the macroradicals are terminated by radicals directly formed from the initiator, and when the monomer is involved in the initiation step(28).

The persulfate ion is known to act as a strong oxidizing agent in aqueous solution. Persulfate, either alone or with activators, has been extensively used as an initiator of vinyl polymerization. Persulfate ion in aqueous solution, when is heated alone or in the presence of a reducing agent(catalyst), decomposes to sulfate radical ions (as shown in equations 10 and 11) which affect its subsequent reactions(4,7,10,33):

for thermal initiation

$$S_2O_8^{2-} \quad \text{---------}> \quad 2SO_4^{-\cdot} \qquad \text{eq.10}$$

for redox initiation

$$S_2O_8^{2-} + R \quad \text{---------}> \quad SO_4^{2-} + SO_4^{-\cdot} + R^{+\cdot} \qquad \text{eq.11}$$

R is a reducing agent.

Ito, K. and his coworkers (therein 28) studied the solution polymerization of acrylic acid in water, at low concentration, as a function of pH of the monomer mix(acrylic acid and sodium acrylate). The rate of polymerization with the rate constant proportional to the square root of initiator concentration. Polymerization rate initially fell over the pH range of 2-7, then rose slowly from pH 7 to 12, but a complete rate equation was not proposed.

4.6 Effect of KCl and MgCl$_2$ Solutions on Water Absorbency of the Copolymer

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 concentration (34). The water intake by the gel reduced the osmotic pressure until an ion concentration equilibrium was reached. The highest water-absorbing copolymer obtained in Section 3.2.3 (water absorbency = 347 g/g) was selected to test the salt effect in various concentrations of KCl and MgCl$_2$ solutions. The influences of KCl and MgCl$_2$ upon the water absorbency of the copolymer are summarized in Table 4.6 and Figure 4.4.

A water absorbent system consists of a quantity of polymer network with a variable quantity of aqueous component. The osmotic pressure attributable to the polymer network is the driving force for the water absorption and, consequently, swelling. At swelling equilibrium, the chemical potentials of water in the polymer equals that of water surrouding the polymer. Addition of a simple salt to the polymer solution leads to network contraction as indicated by viscosity lowering and the decreasing of the chemical potential of the water surrounding a polyelectrolyte polymer. Therefore, absorbent polyelectrolyte polymers cannot imbibe as much salt water as

pure water(31).

TABLE 4.6

Effect of Different KCl and MgCl$_2$ Concentrations
on Water Absorbency of the Copolymer

Concentration of Salt Solution (% wt/v)	Water Absorbency (g H$_2$O/g dry polymer)	
	in KCl Solution	in MgCl$_2$ Solution
0	347	347
0.1	46	11
0.5	20	5
1.0	13	4
2.0	12	1

The result shows the tendency that the water absorbency decreases as the salt concentration increases due to the ionic strength (I) of the salt solution. The ion concentration and ionic strength of the salt solutions are calculated in Table 4.7.
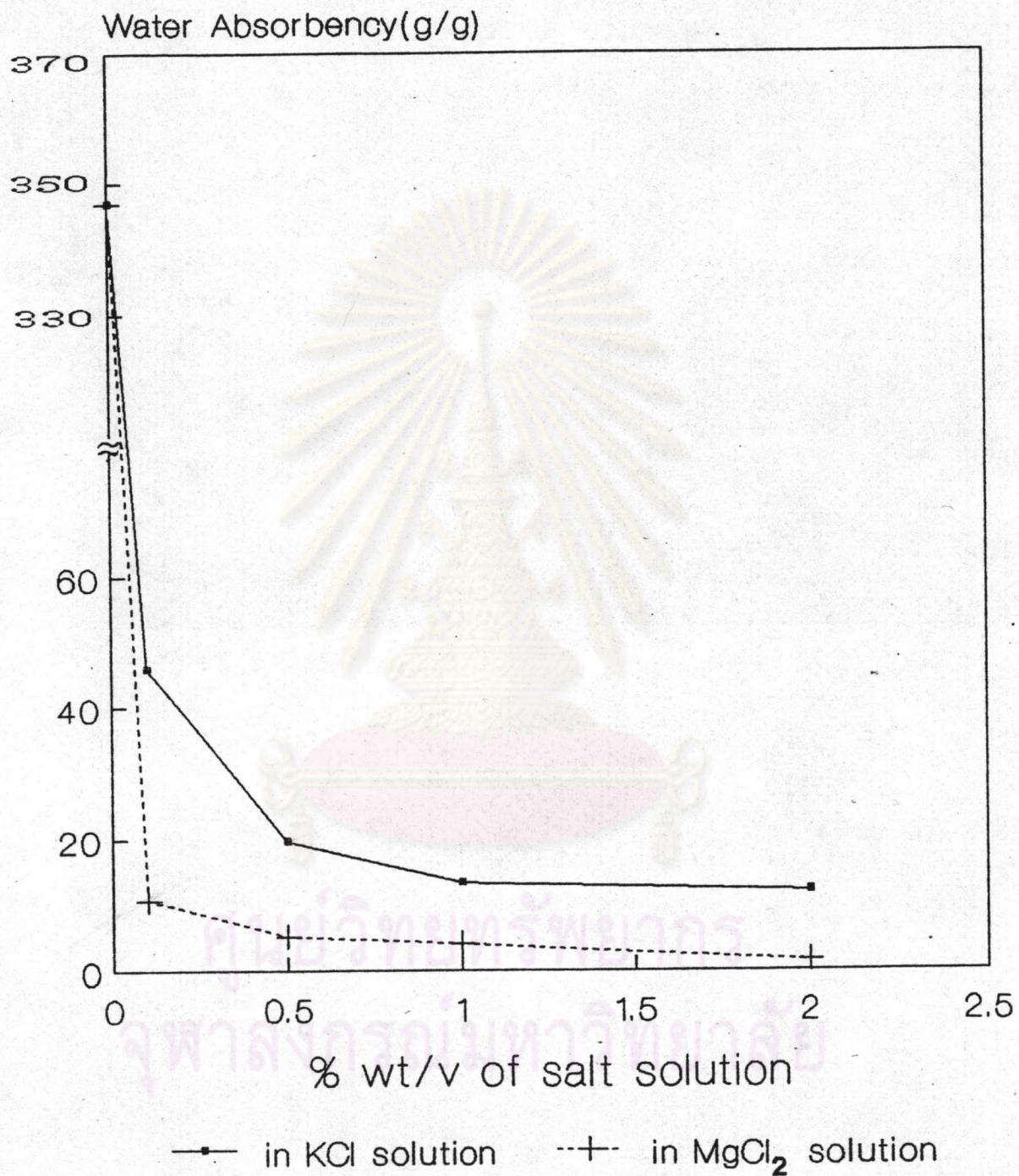
FIGURE 4.4 Effect of different KCl and MgCl$_2$ concentrations
on water absorbency of the copolymer

TABLE 4.7

Ion Concentration and Ionic Strength of the Salt Solution

Contration of Salt Solution (%wt/v)	Ion Concentration				Ionic[*] Strength (mole-ion/dm^3)	
	in KCl(aq)		in MgCl$_2$(aq)		KCl(aq)	MgCl$_2$(aq)
	K^+	Cl^-	Mg^{2+}	Cl^-		
0.1	0.0134	0.0134	0.0105	0.0210	0.0134	0.0315
0.5	0.0670	0.0670	0.0525	0.1050	0.0670	0.2010
1.0	0.1340	0.1340	0.1050	0.2100	0.1340	0.4020
2.0	0.2680	0.2680	0.2100	0.4200	0.2680	0.8040

[*] $I = 1/2\ C_i Z_i^2$; where I, C_i and Z_i are the ionic strength, the ionic concentration and the charge on each individual ion, respectively(35).

On observing the case of MgCl$_2$, the water absorbency decreased even more with increasing MgCl$_2$ concentrations. This suggests that the equilibrium osmotic pressure is reached earlier in the presence of the divalent ion as result of the higher ionic strength of the MgCl$_2$ solution comparing with that of KCl solution at the same concentration. In addition, the divalent Mg^{2+} ions may crosslink the gel by salt formation with the carboxylate groups on adjacent chains or chain segments of the copolymer. Consequently, the crosslink density of the network increases (34,36,37).

4.7 Characterization

4.7.1 Study of the Functional Groups in the Copolymer

The functional groups in the copolymer were investigated by IR. The spectrum was shown in Figure 4.5 and interpreted in Table 4.8.

The result shows that the IR spectrum of the copolymer was similar to that of the hydrolysed polyacrylamide (38).

TABLE 4.8

The Assignment for the IR spectrum

of the poly(acrylamide-*co*-potassium acrylate)

Wave number (cm^{-1})	Assignment
3800-3300	O-H stretching
3200	N-H stretching
2920, 2840	aliphatic C-H stretching
1660, 1610	C=O stretching of the $-CONH_2$
1560	C=O asymmetric stretching for the carboxylate ion
1450	C-H asymmetric bending
1400	C=O symmetric stretching for the carboxylate ion
1315	C-N aliphatic stretching

4.7.2 Structure of the Copolymer

The copolymer was subjected to analyse the structure by ^{13}C-Solid State NMR as shown in Figure 4.6.   The spectrum shows two
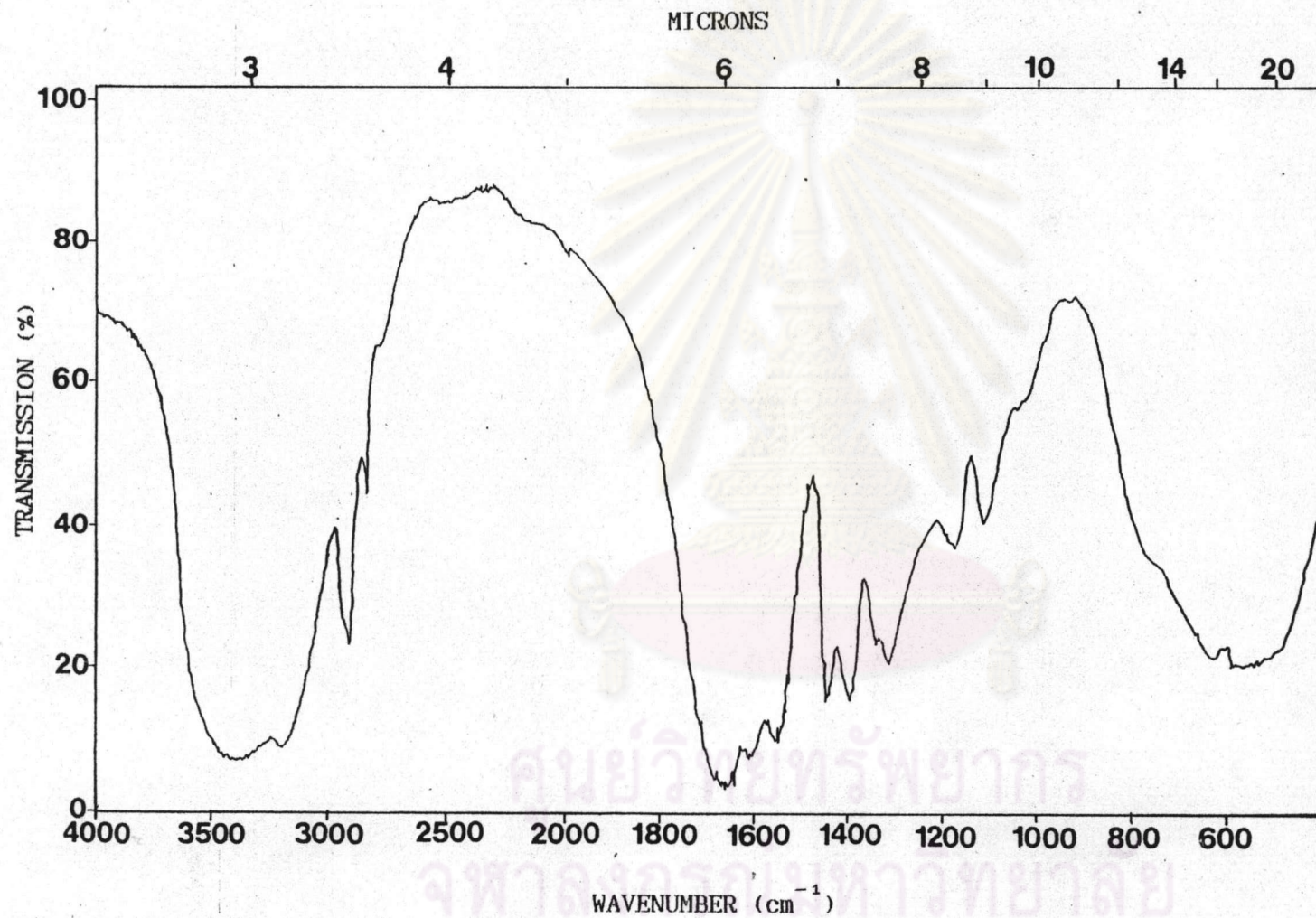
FIGURE 4.5 IR spectrum of the poly(acrylamide-*co*-potassium acrylate)

13C CP/MAS, SSB = 3901HZ, INSERT, SAMPLE P 56

PPM

180.107

42.386
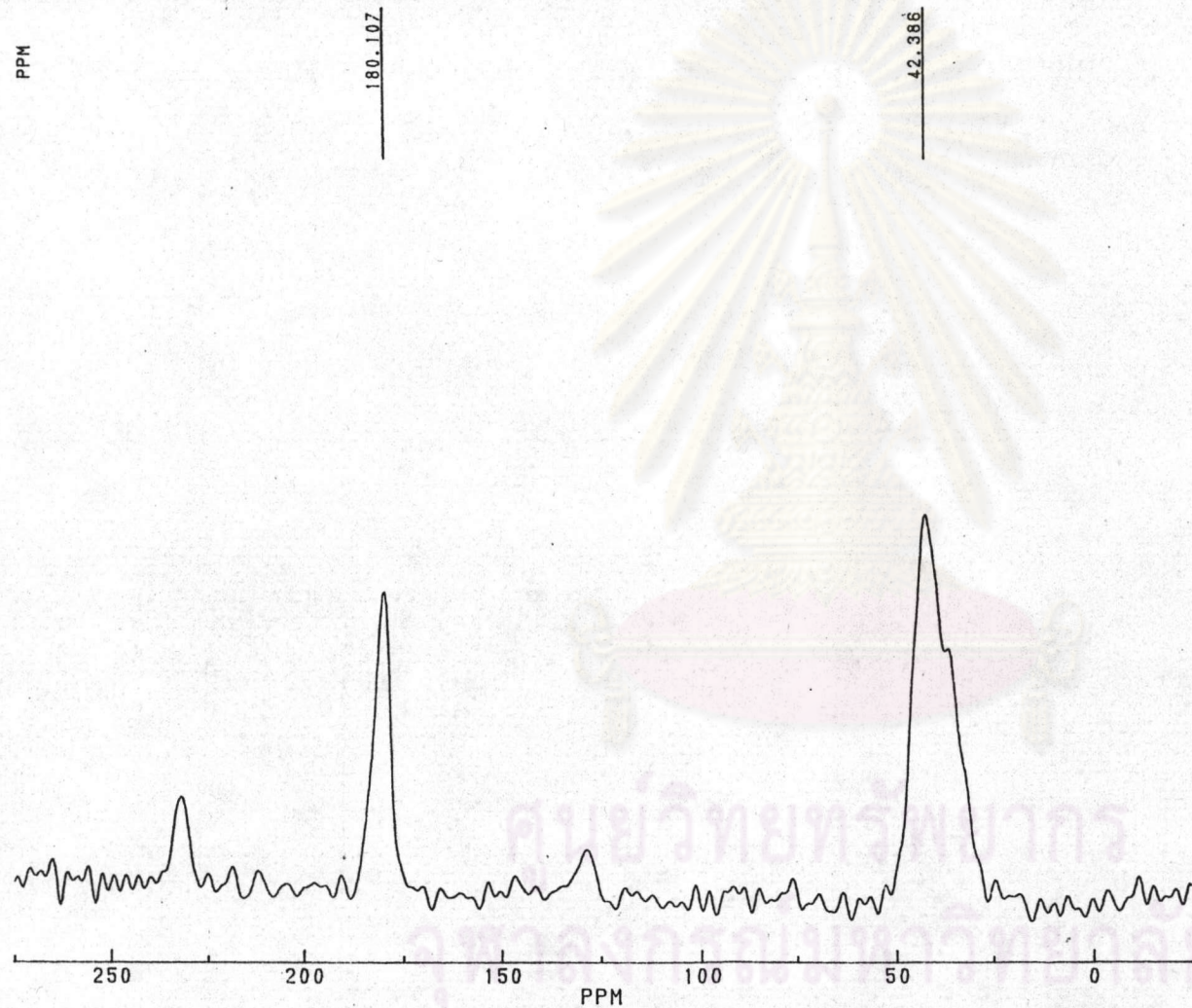
CHEMALT.003
PPG:
  CPCYCL.PC

SF   75.470
O1   13000.000
SI   2048
TD   256
SW   29411.765
HZ/PT   28.722

RG   25
NS   504

DW   17.0
O2   21000.000
DP   9H DO

D0   8.000S
D1   5.000U
D3   35.000U
D5   5.000M
D7   820.000M
D11   5.000U

LB   0.0
SR   3181.10

PPM

FIGURE 4.6 ^{13}C-Solid State NMR spectrum of the copolymer

main peaks which correspond to the signals of the carbonyl C and aliphatic C (of the polymer backbone) at the chemical shifts 180.107 and 42.386 ppm, respectively. In order to obtain a high-resolution NMR spectrum, the water-soluble copolymer obtained from Section 3.3.1 was analysed with an FT-NMR in the modes of ^{1}H-NMR and ^{13}C-NMR. The ^{1}H-NMR spectrum in Figure 4.7 shows three characteristic peaks at 1.39, 1.97, and 4.68 ppm corresponding to the proton signals of $-CH_2$, $-CH$, and $-NH$, respectively. The ^{13}C-NMR spectrum of the water-soluble copolymer illustrated in Figure 4.8 shows three signals at 179.11, 41.24, and 33.84 ppm corresponding to the C=O, $-CH$, and $-CH_2$ groups, respectively.

To be able to observe the pattern of the carbonyl carbon (39) of the water-soluble copolymer, the ^{13}C-NMR spectrum was expanded in the 173-185 ppm region as shown in Figure 4.9. The spectrum indicates that the microstructure of the copolymer consists of polyacrylamide (MMM) homopolymer and copolymers(MMA, AMA), so the phase separation should exist in the copolymer. It is very common that homopolymer formation always accompanies the graft copolymerization reaction.

4.7.3 Study of Thermal Properties of the Copolymer

In addition, the copolymer was investigated by DSC to identify T_g and T_m of the copolymer. The DSC thermogram of the copolymer as depicted in Figure 4.10 shows two endothermic peaks. Hence, the phase separation should exist in the copolymer. The T_{g1} and T_{m1} of the copolymer are 74.77 $^{\circ}$C and 127.11 $^{\circ}$C while T_{g2} and T_{m2} exist at 193.52 and 245.08 $^{\circ}$C, respectively. The T_{g2} at 193.52 $^{\circ}$C correlates to the T_g value of poly(potassium acrylate) (194 $^{\circ}$C) in the literature(30). But the T_{g2} of the copolymer is far lower than the reference T_g value of polyacrylamide (165 $^{\circ}$C) probably due to the
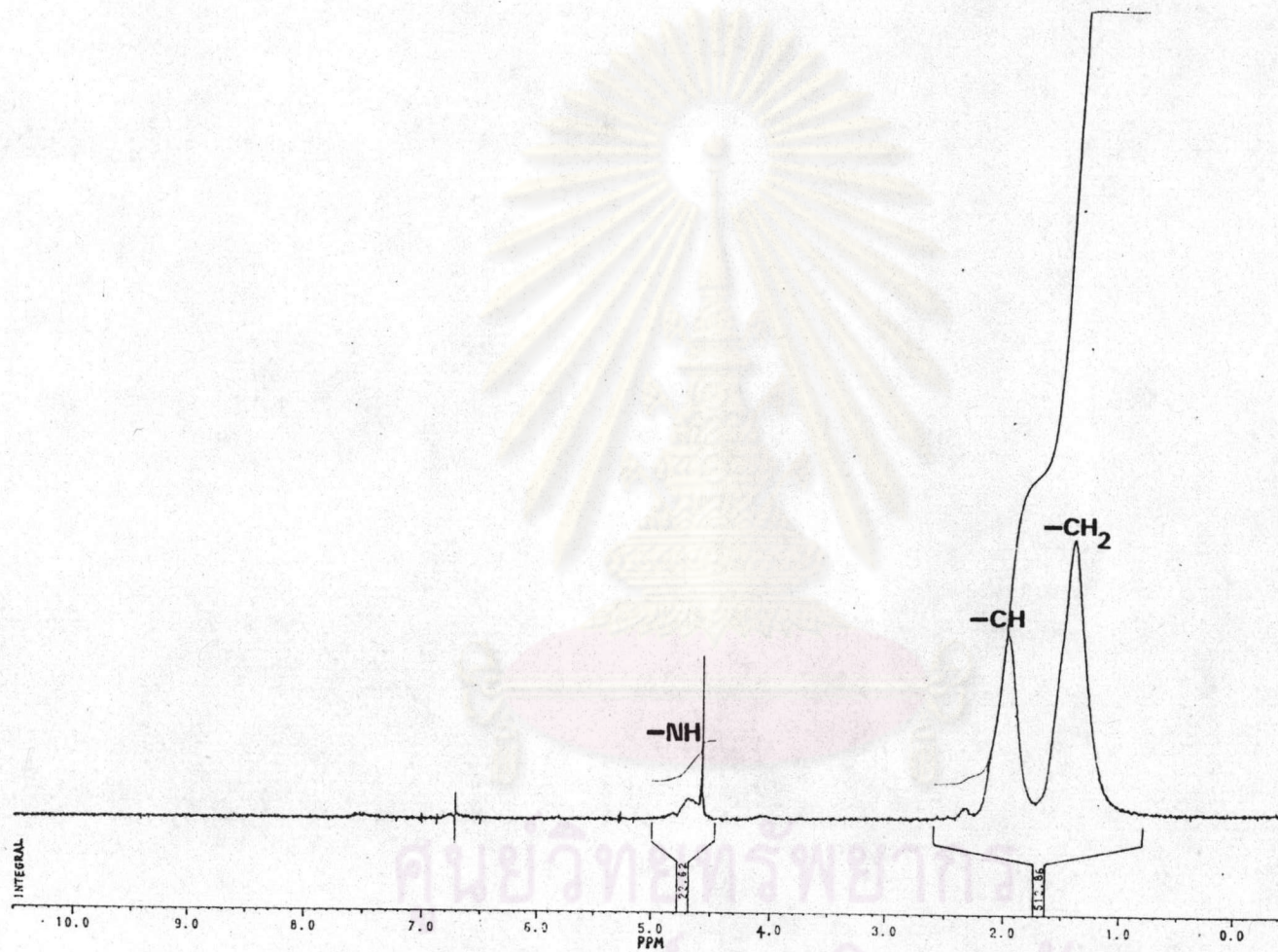
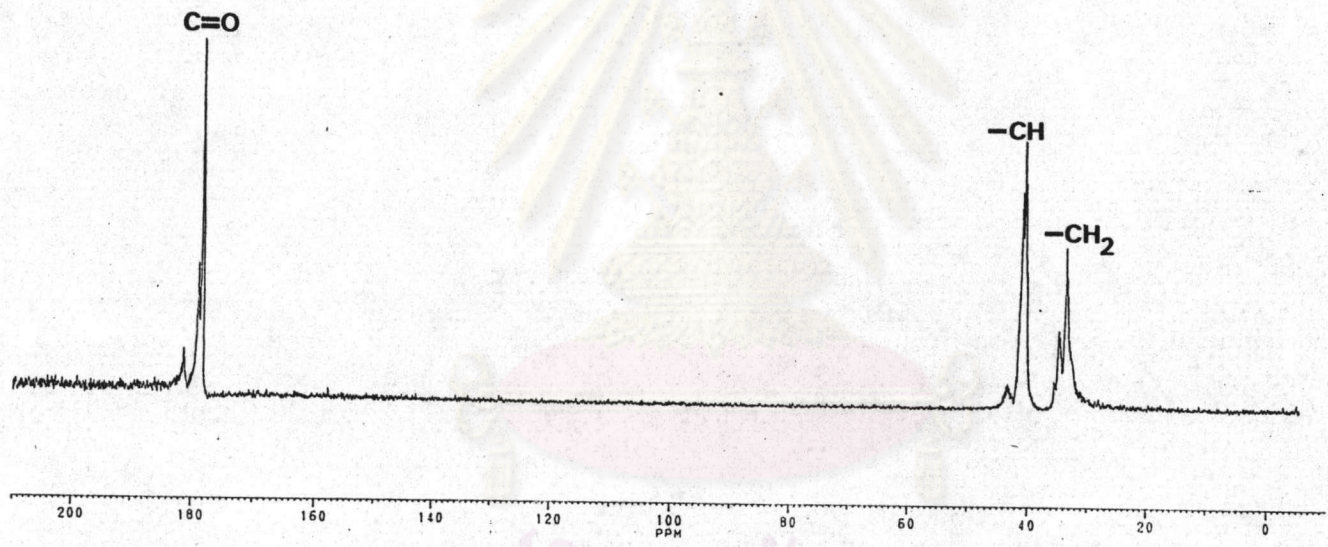FIGURE 4.7 ^{1}H-NMR spectrum of the water-soluble copolymer

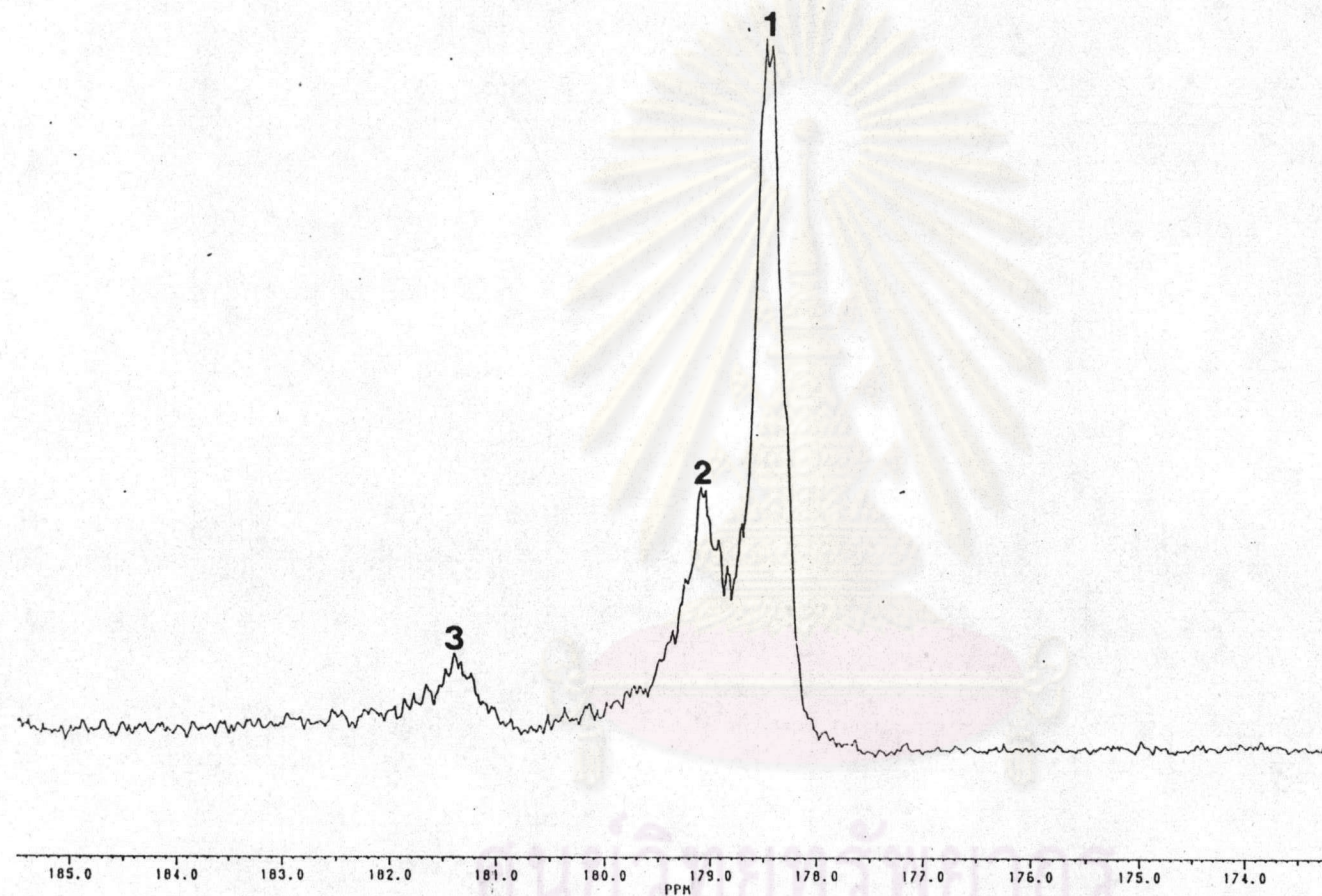FIGURE 4.8 ^{13}C-NMR spectrum of the water-soluble copolymer

FIGURE 4.9   ^{13}C-NMR spectrum of the carbonyl carbon of the water-soluble copolymer.   The   number   on the spectrum identify monomer triads: (1) MMM (178.49 ppm); (2) MMA (179.11 ppm);(3) AMA (181.40 ppm) where M represents an acrylamide unit and A is an acrylate unit.

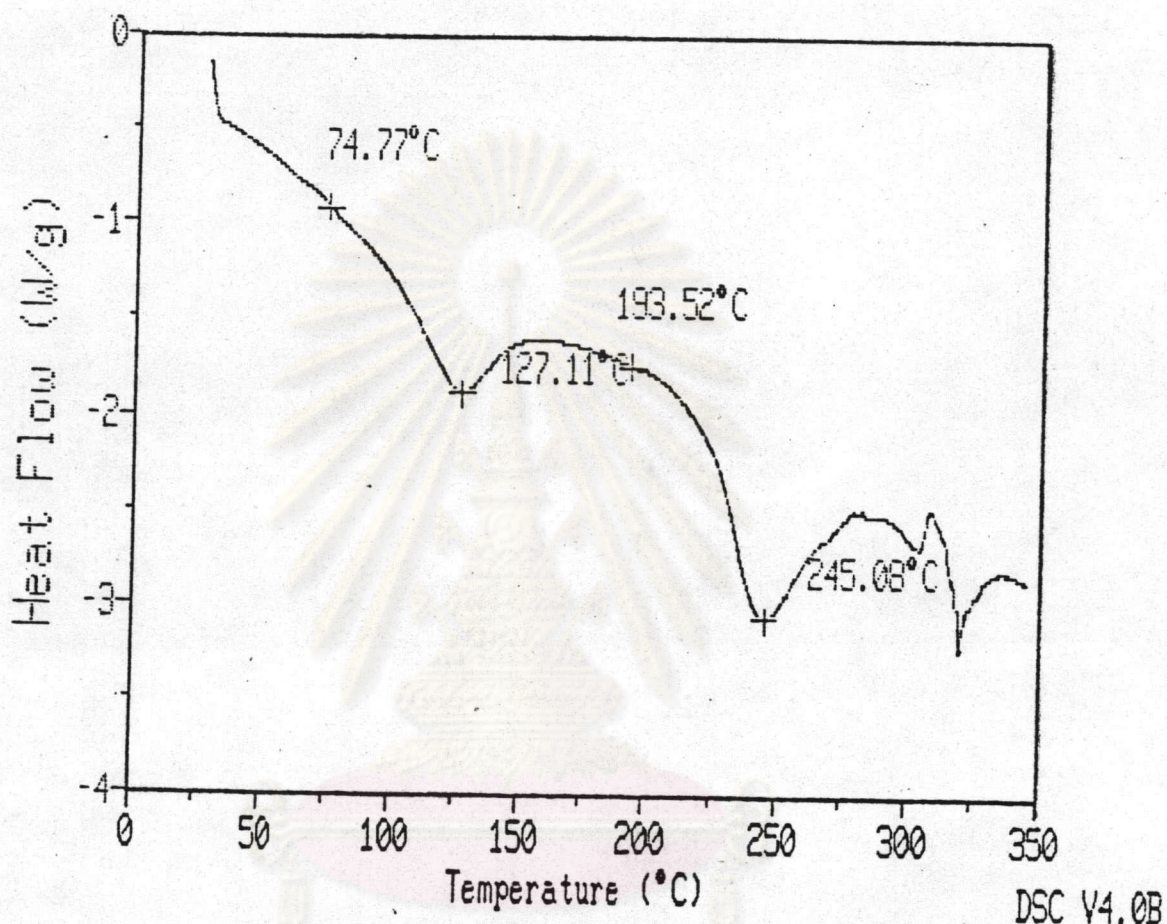interference of the coating of Span 60 on the surface of the copolymer beads.

FIGURE 4.10   DSC thermogram of the copolymer

4.7.4 Surface Morphology of the Copolymer Beads

Moreover, the copolymer beads were photographed by SEM to observe the surface appearance. The electron micrographs of the water-soluble and crosslinked copolymer are shown in Figures 4.11 and 4.12, respectively.   From the SEM micrographs, lumps are observed on the water-soluble copolymer whereas the crosslinked copolymer beads are rather round in appearance.   The cellular structure found in the

15KU   X500   50μm   004262

FIGURE 4.11   SEM micrograph of the water-soluble copolymer
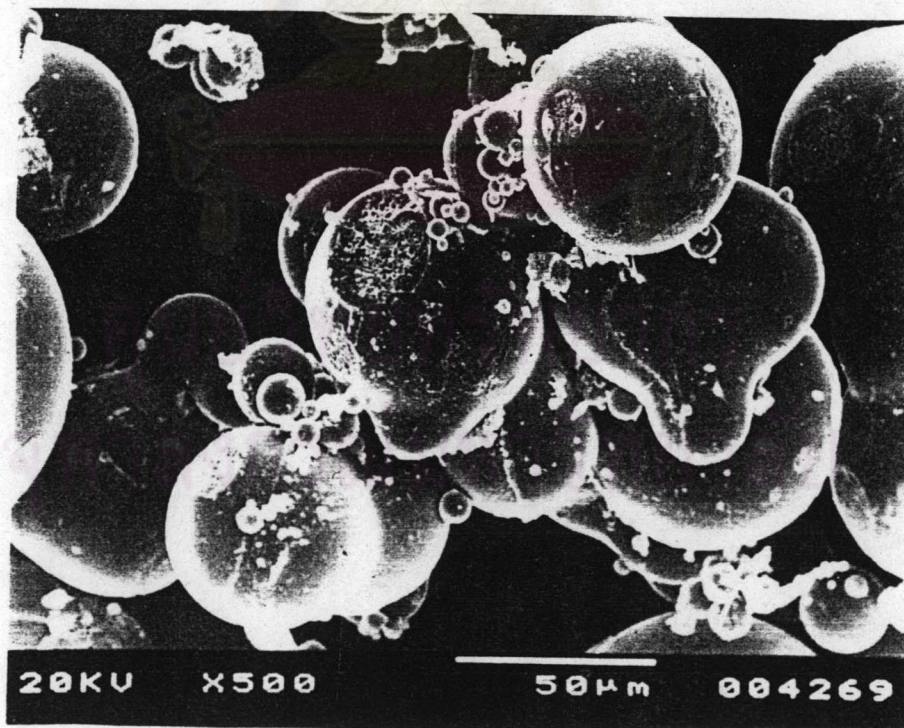

20KU   X500   50μm   004269

FIGURE 4.12   SEM micrograph of the crosslinked copolymer

crosslinked copolymer as shown in Figure 4.13 is similar to that of a polyacrylamide gel (Figure 4.14) (40). The occurrence of the cellular structure may be due to the high molar ratio of acrylamide used in polymerization to produce polyacrylamide networks.
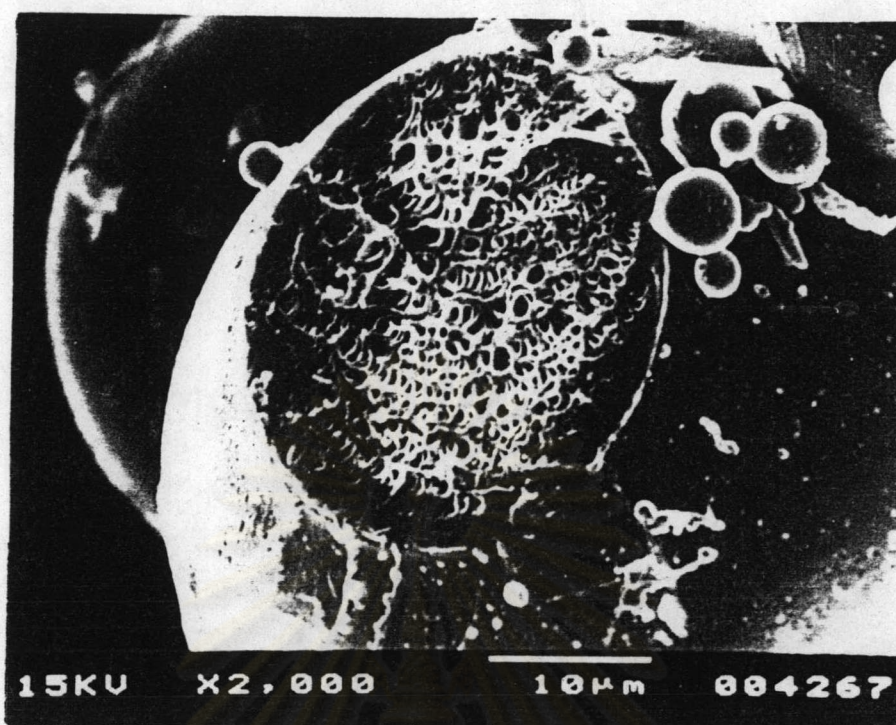
FIGURE 4.13 Scanning electron micrograph showing the cellular
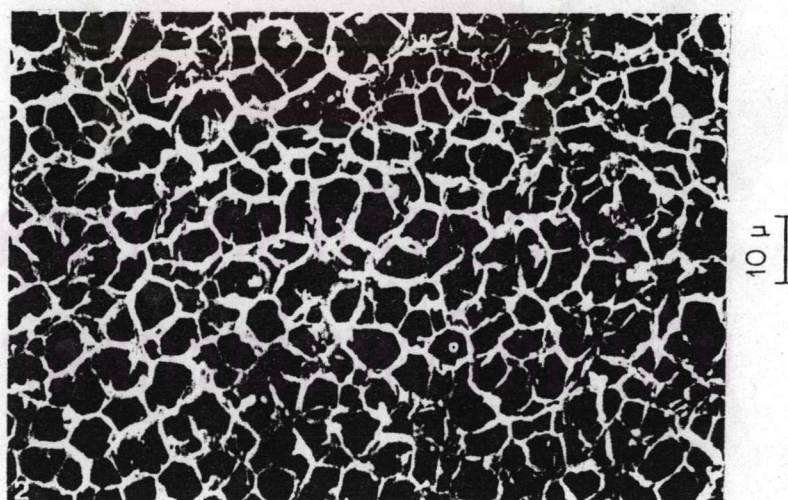structure of the copolymer bead

FIGURE 4.14 Scanning electron micrograph showing the cellular structure
of a polyacrylamide gel.(The figure is reproduced from Reference 39.)