CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization the functional groups of the copolymer by FTIR

The functional groups of the synthesized copolymer were investigated by FTIR. The spectrum is shown in Figure 4.1 and Table 4.1.

The result shows that FTIR spectrum of the synthesized copolymer similar to that of the poly(acrylic acid) and polyacrylamide, shown in Figures 4.2 and 4.3, respectively. The spectrum of copolymer confirms the existence of the carboxylate and carboxamide functionalities.

Table 4.1

Assignments for the FTIR 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

84
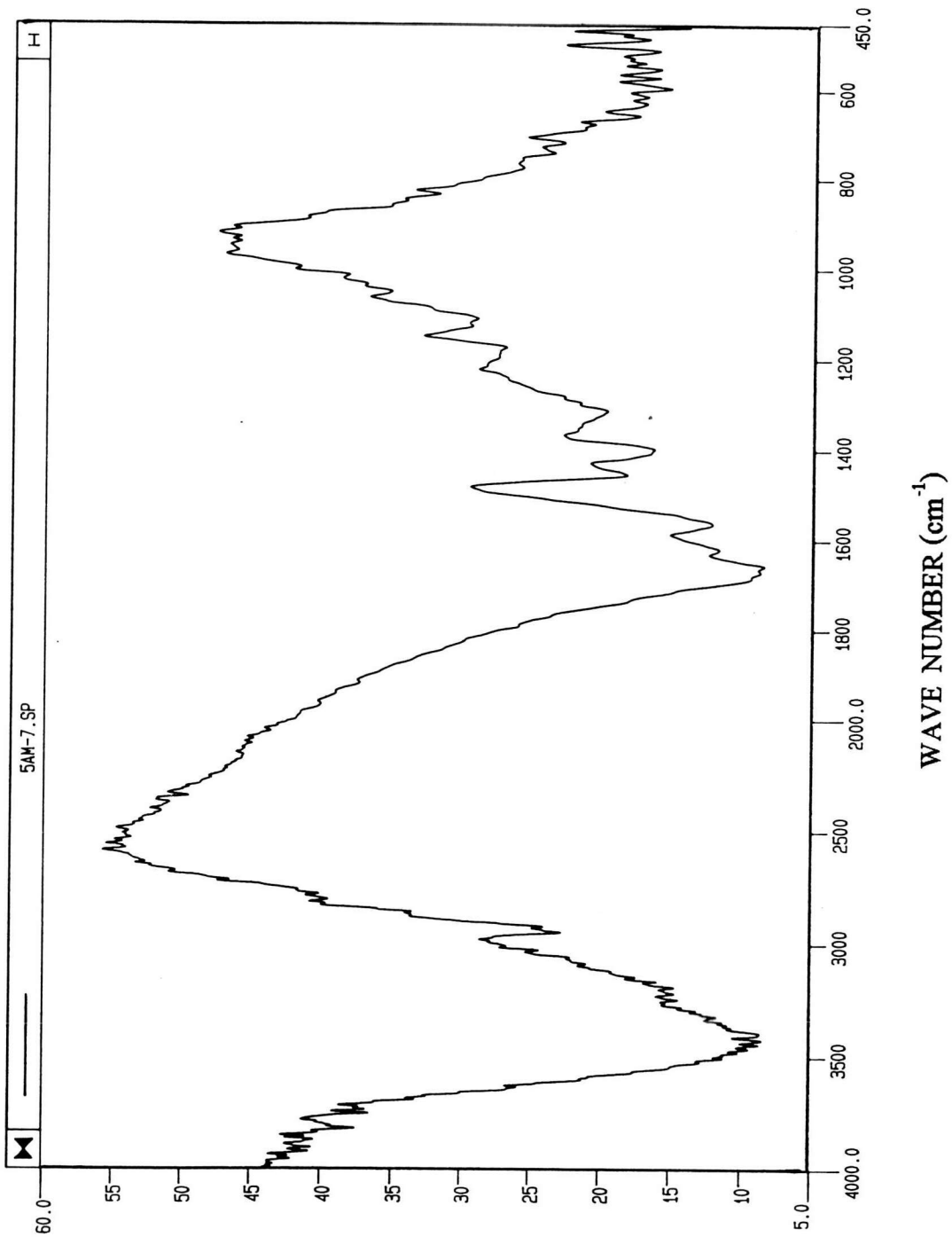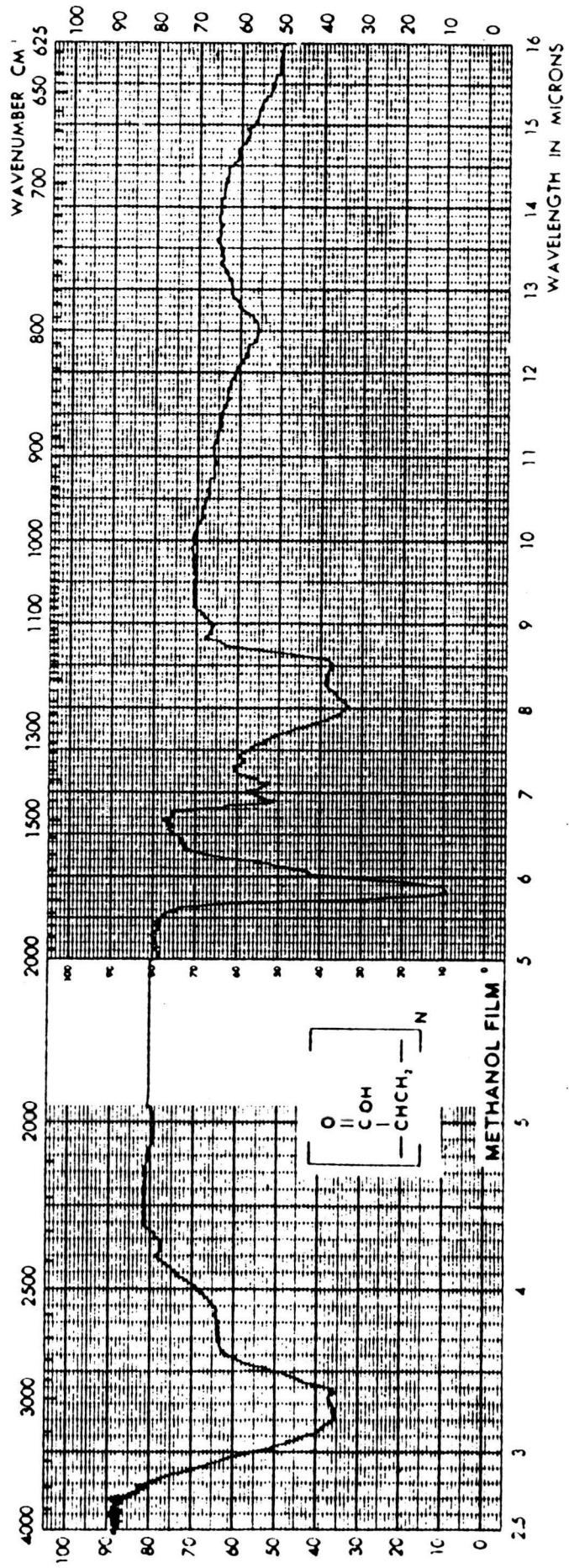

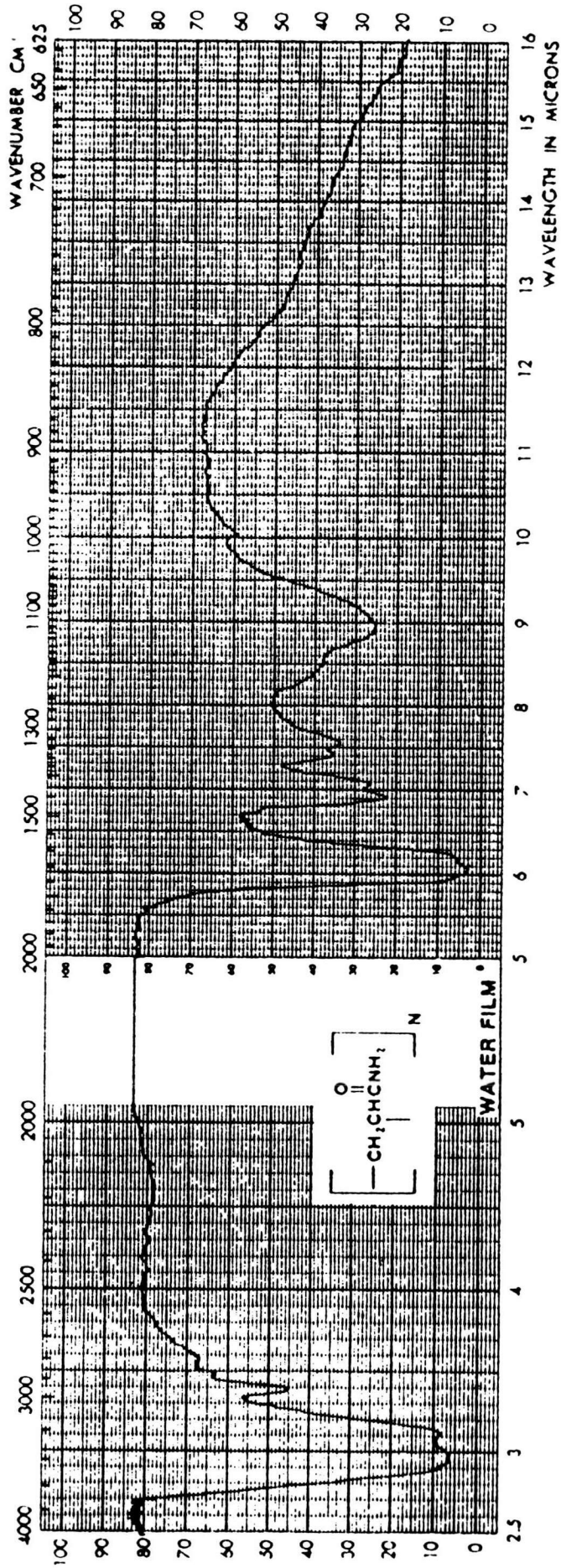Figure 4.1 FTIR Spectrum of the poly(acrylamide-co-potassium acrylate)

85

WAVE NUMBER (cm⁻¹)

Figure 4.2 FTIR Spectrum of the polyacrylic acid

18,127-7
Poly(acrylamide)
Granular

$\begin{bmatrix} CH_2CHCNH_2 \\ | \\ O=C \end{bmatrix}_N$

WATER FILM

WAVENUMBER CM⁻¹

WAVELENGTH IN MICRONS

WAVE NUMBER (cm⁻¹)

Figure 4.3 FTIR Spectrum of the polyacrylamide

Table 4.1

Assignments for the FTIR spectrum of the

poly(acrylamide-co-potassium acrylate) (continued)

Wave number (cm^{-1})	Assignment
1450	C-H asymmetric bending
1400	C═O asymmetric stretching for the carboxylate ion
1315	C-N aliphatic stretching

4.2 The optimum total concentration, the molar ratio of monomer solution and the cross-linking agent concentration

The result of water absorbency test and vortex test of the copolymer beads, synthesized by inverse suspension polymerization with various total concentrations of monomer solutions, molar ratio of monomer concentrations of potassium acrylate(KA), and acrylamide(AM), and the cross-linking agent concentration was in Tables 4.2-4.5 and Figures 4.4- 4.6.

The synthesized copolymers of AM and KA are swollen in water on the account of the hydrophilic pendants (amide and carboxylate groups) in their structure, especially the synthesized copolymer, which molar ratio of AM:KA at 60:40 and the total concentration monomer solution of 5 molar at 0.025% mole cross-linking agent, N,N$'$-MBA, produced the water insoluble beads with high-water absorbency values of 775 times its dry weight and a high water absorption speed(21.41 sec.). The water absorption ability and the water absorption speed were decreased with increasing the total monomer concentration and the cross-linking agent concentration because chain transfer to polymer was increased with

Table 4.2

Effect of the total monomer concentration and molar ratio of the monomers on the water absorbency and water absorption speed

of the synthesized copolymer, in the absence of the cross-linking agent

Molar ratio of KA : AM	Total monomer concentration (Molar)					
	5 M		7 M		10 M	
	water absorbency (g/g)	vortex time (sec)	water absorbency (g/g)	vortex time (sec)	water absorbency (g/g)	vortex time (sec)
10 : 90	soluble	> 200	766 ± 116	89.20	soluble	78.79
20 : 80	soluble	> 200	778 ± 146	63.41	645 ± 111	71.20
30 : 70	59 ± 9	> 200	778 ± 56	50.48	762 ± 59	50.25
40 : 60	1484 ± 403	59.31	825 ± 88	41.26	743 ± 51	39.80
50 : 50	673 ± 181	35.21	617 ± 75	26.52	762 ± 45	30.84
60 : 40	725 ± 47	33.55	541 ± 35	52.91	840 ± 128	30.40
70 : 30	769 ± 175	27.31	478 ± 90	43.83	576 ± 60	21.61
80 : 20	956 ± 360	29.30	420 ± 64	29.24	618 ± 77	20.27
90 : 10	834 ± 239	26.41	365 ± 40	27.10	619 ± 16	15.82

Table 4.3

Effect of the total monomer concentration and molar ratio of the monomers on the water absorbency and water absorption speed of the synthesized copolymer, in the presence of N,N'-MBA, cross-linking agent concentration = 0.025 % mole of monomer

Molar ratio of KA : AM in feed	Molar ratio* of KA : AM in copolymer	Total monomer concentration (Molar)					
		5 M		7 M		10 M	
		water absorbency (g/g)	vortex time (sec)	water absorbency (g/g)	vortex time (sec)	water absorbency (g/g)	vortex time (sec)
10 : 90	10.76 : 89.24	456 ± 30	39.38	232 ± 4	44.28	201 ± 15	42.14
20 : 80	19.06 : 80.95	629 ± 22	35.13	305 ± 9	37.13	299 ± 24	36.89
30 : 70	25.56 : 74.43	661 ± 78	29.95	417 ± 20	22.56	405 ± 11	31.10
40 : 60	37.79 : 62.21	775 ± 99	21.41	429 ± 15	25.10	499 ± 28	26.23
50 : 50	43.12 : 56.88	525 ± 28	25.54	512 ± 25	26.58	410 ± 31	23.19
60 : 40	52.85 : 47.15	612 ± 22	42.74	487 ± 39	30.94	401 ± 46	19.93
70 : 30	63.25 : 36.75	575 ± 72	23.07	457 ± 43	34.84	375 ± 29	18.65
80 : 20	77.57 : 22.43	584 ± 31	20.17	374 ± 21	24.52	350 ± 24	19.93
90 : 10	87.89 : 12.10	582 ± 27	18.24	356 ± 19	19.43	342 ± 14	17.38

* Molar ratio of KA : AM was checked by Elemental Analysis method

Table 4.4

Effect of the total monomer concentration and molar ratio of the monomers on the water absorbency and water absorption speed

of the synthesized copolymer, in the presence of N,N′-MBA, cross-linking agent concentration = 0.05 % mole of monomer

Molar ratio of KA : AM	Total monomer concentration (Molar)					
	5 M		7 M		10 M	
	water absorbency (g/g)	vortex time (sec)	water absorbency (g/g)	vortex time (sec)	water absorbency (g/g)	vortex time (sec)
10 : 90	335 ± 1	43.21	179 ± 4	44.85	97 ± 2	41.21
20 : 80	447 ± 26	40.83	255 ± 9	40.21	169 ± 11	36.61
30 : 70	537 ± 53	33.20	276 ± 31	39.86	185 ± 12	30.24
40 : 60	568 ± 27	28.35	244 ± 4	17.81	159 ± 3	27.36
50 : 50	558 ± 50	18.38	270 ± 19	11.48	215 ± 2	23.19
60 : 40	544 ± 55	22.97	244 ± 2	37.71	145 ± 2	20.76
70 : 30	519 ± 92	16.19	233 ± 1	14.96	170 ± 3	14.21
80 : 20	386 ± 21	14.80	226 ± 3	11.31	143 ± 2	12.34
90 : 10	319 ± 4	14.21	204 ± 4	10.76	133 ± 5	8.43

Table 4.5

Effect of the total monomer concentration and molar ratio of the monomers on the water absorbency and water absorption speed

of the synthesized copolymer, in the presence of N,N′-MBA, cross-linking agent concentration = 0.075 % mole of monomer

Molar ratio of KA : AM	Total monomer concentration (Molar)					
	5 M		7 M		10 M	
	water absorbency (g/g)	vortex time (sec)	water absorbency (g/g)	vortex time (sec)	water absorbency (g/g)	vortex time (sec)
10 : 90	269 ± 12	28.19	139 ± 5	29.14	61 ± 2	27.23
20 : 80	439 ± 9	23.59	204 ± 1	25.81	86 ± 4	26.28
30 : 70	476 ± 15	21.89	244 ± 6	25.87	121 ± 3	24.17
40 : 60	519 ± 32	16.70	268 ± 5	21.89	158 ± 13	20.93
50 : 50	471 ± 8	23.51	300 ± 26	15.14	140 ± 21	21.11
60 : 40	385 ± 7	18.53	350 ± 65	40.21	123 ± 15	18.37
70 : 30	484 ± 14	21.48	286 ± 36	16.31	104 ± 20	15.21
80 : 20	483 ± 5	18.26	296 ± 2	15.74	98 ± 14	13.49
90 : 10	400 ± 6	13.41	275 ± 17	14.38	91 ± 5	10.93

monomer concentration, especially at high extents of conversion, and this results in increasing amounts of branching and self-crosslinking reactions that affect product properties [18].

The water absorbency of the cross-linked copolymers, synthesized with various molar ratios of AM:KA to different total monomers concentrations by 1.4 g/l(6.14×10^{-3} M) $(NH_4)_2S_2O_8$ at various concentrations of N,N$'$-MBA were shown in Figures 4.4- 4.6.
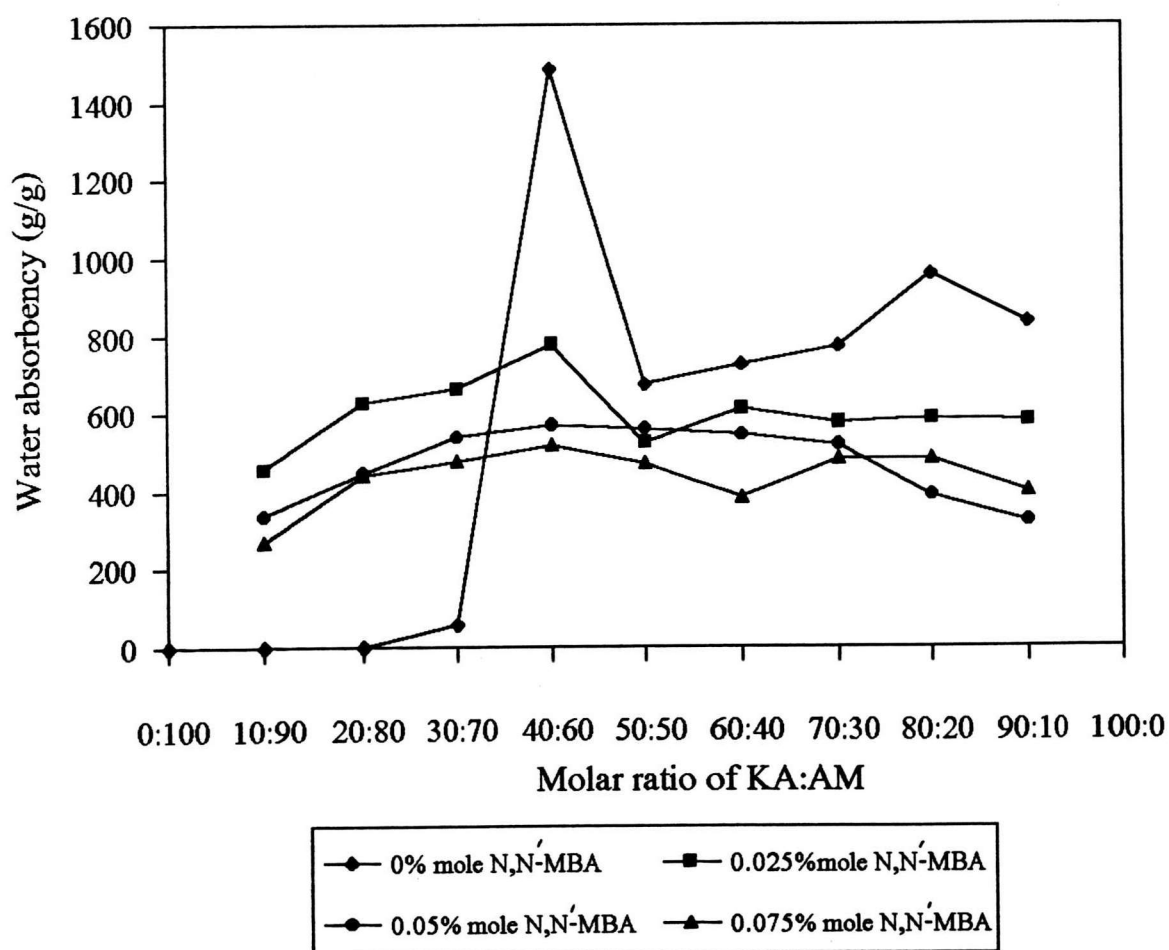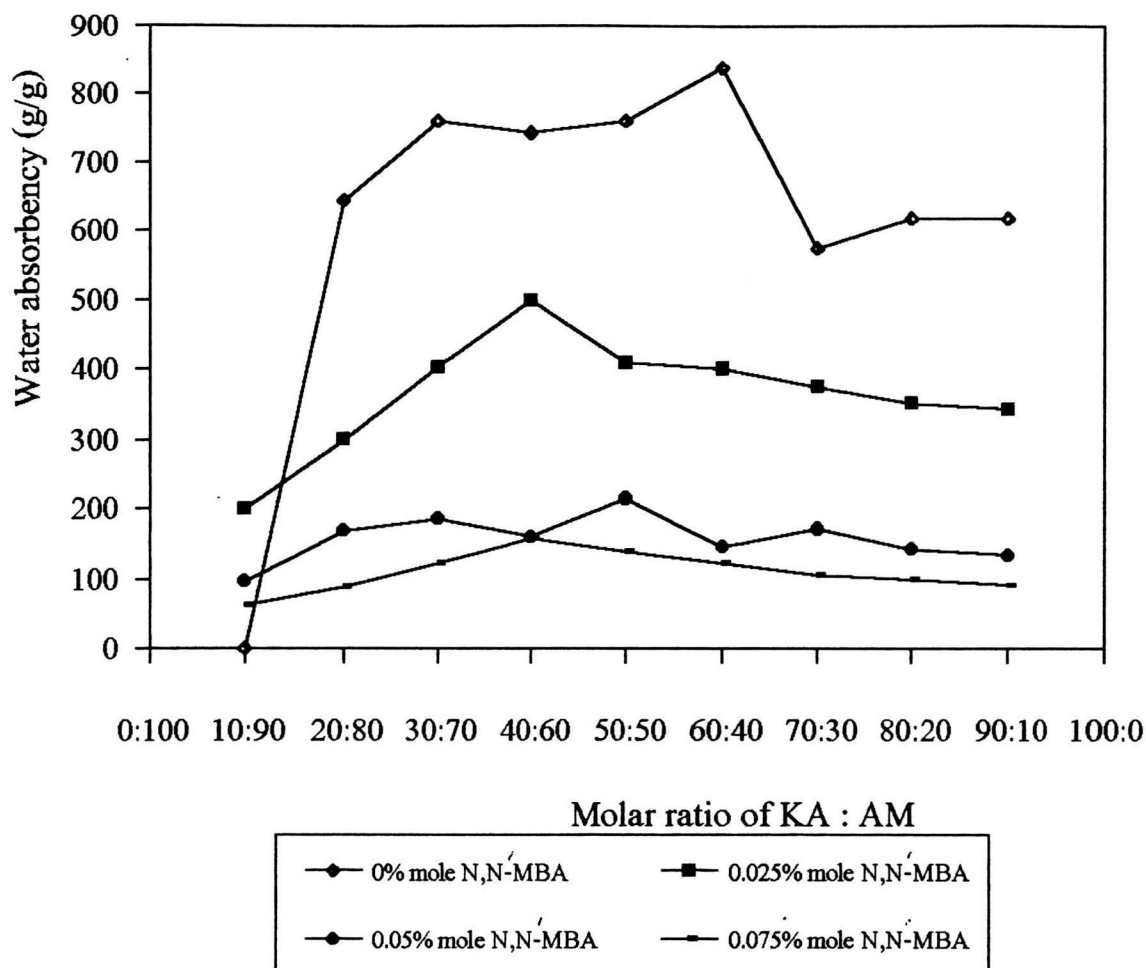

Figure 4.4 Effect of the cross-linking agent on the water absorbency of the synthesized copolymers at various molar ratios of the monomers when the total monomer concentration = 5 M
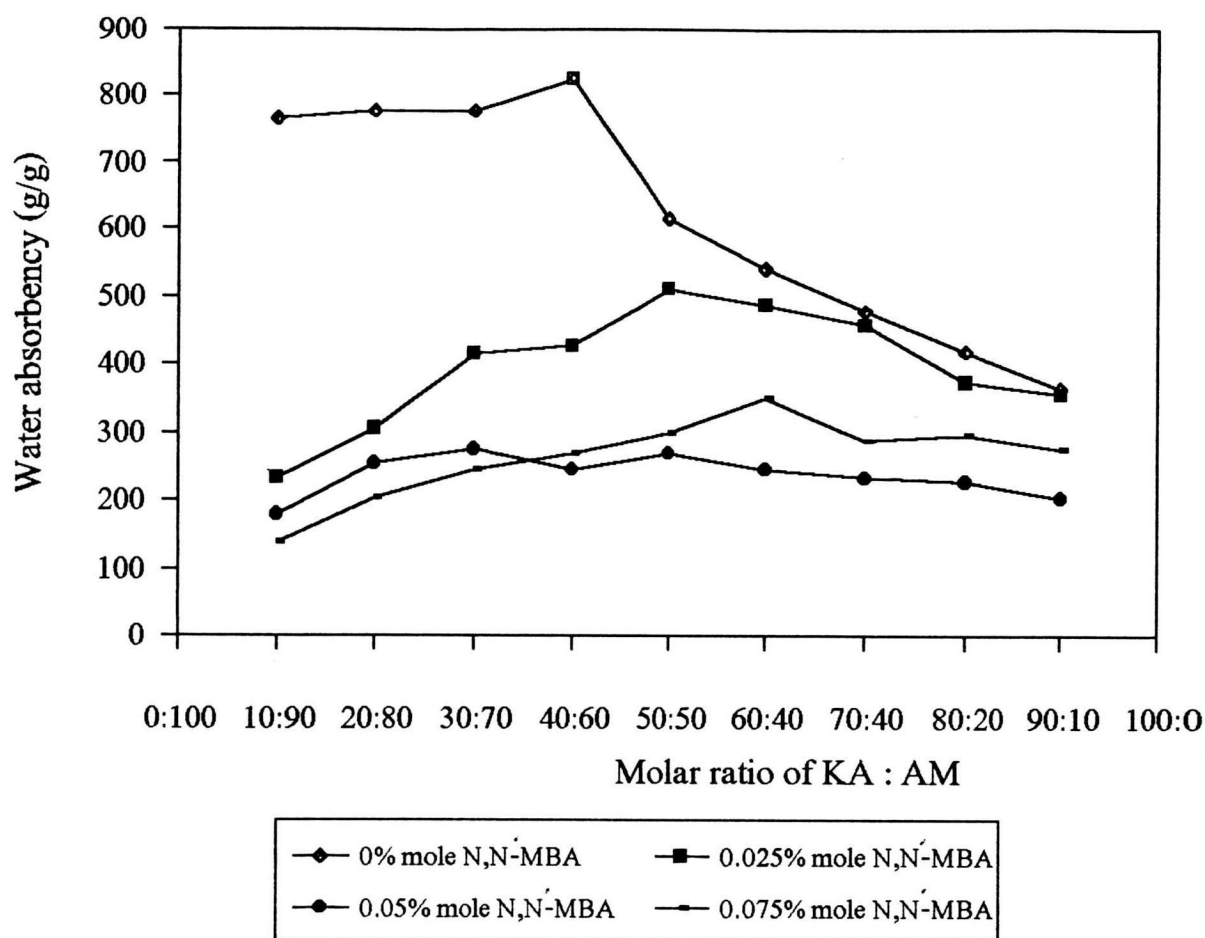
Figure 4.5 Effect of the cross-linking agent on the water absorbency of the synthesized copolymers at various molar ratios of the monomers when the total monomer concentration = 7 M

Figure 4.6 Effect of the cross-linking agent on the water absorbency of the synthesized copolymers at various molar ratios of the monomers when the total monomer concentration = 10 M

The copolymer cross-linked with N,N$'$-MBA gave the optimum product properties at 0.025% mole N,N$'$-MBA of monomer with a water absorbency value of 775 g/g and high gel strength with a sacrification of water absorption, i.e. the extent of water absorption is lower than those of the water absorbing copolymers synthesized in the absence of the cross-linking agent, because the formation of more cross-links that lowers the swelling of the gel. In general,

cross-linking agents have been employed to help improve the gel strength of the swollen gel but it is very effective to reduce the water absorbency.
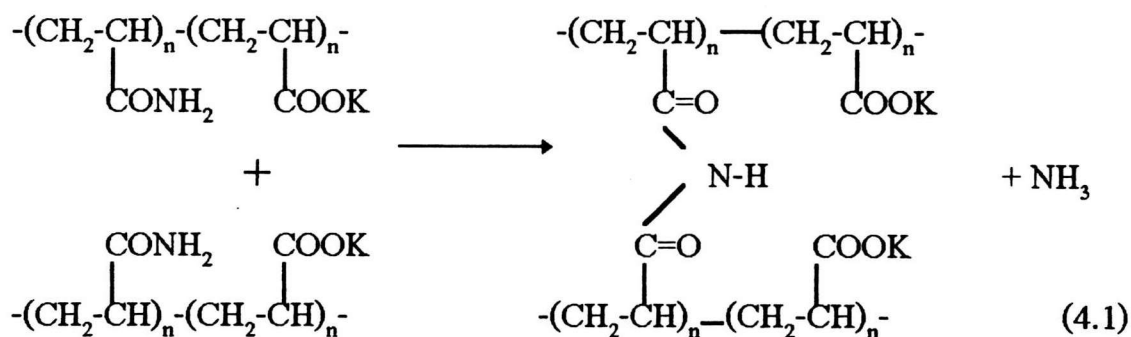
The critical molar ratio of AM:KA at 60:40 produced the optimum superabsorbent polymer; this indicates that one of the side reactions could be cross-linking of the copolymer with an appropriate cross-linking agent whose concentration is 0.025% mole of monomer. Actually, the structure of the copolymer should consist of more acrylate units than acrylamide units owing to the higher hydrophilicity of the carboxylate group, and the reactivity of KA is higher than that of AM. The copolymerization reactivity ratios of KA and AM are 1.35 and 0.78, respectively [65]. In the contrast, if the flexibility of polymer chains was an important factor, the water absorbency should increase with decreasing concentration of acrylate units in the polymer chain since the glass transition temperature (T_g) of potassium acrylate is higher than that of acrylamide, i.e., 194°C and 165°C, respectively [65, 66].

The water absorbency ability of the all synthesized copolymers containing various ratios of monomer of KA and AM, in the absence of the cross-linking agent was higher than those with the cross-linking agent, because the former contained both soluble and insoluble beads with poor gel strength. The insolubility of the copolymer is possibly due to the formation of a gel in the absence of any cross-linking monomer, which may be described as the following side reactions:

a) polymerizing highly concentrated solutions of acrylic acid, may cause an auto-crosslinking through a hydrogen abstraction from the polymer backbone followed by radical combination [1, 67].

b) chain transfer to polymer may occur during the polymerization[18].

c) the occurrence of imidization that usually takes place in the polymerization of acrylamide in concentrated solution and at high temperature and pH [68]. The imidization of the amide pendants in the copolymer is shown below:

$$-(CH_2\text{-}CH)_n\text{-}(CH_2\text{-}CH)_n- \quad\quad -(CH_2\text{-}CH)_n\text{---}(CH_2\text{-}CH)_n-$$

CONH$_2$	COOK		C=O	COOK

$$+ \quad\quad\quad\quad \text{N-H} \quad\quad\quad\quad + NH_3$$

CONH$_2$	COOK		C=O	COOK

$$-(CH_2\text{-}CH)_n\text{-}(CH_2\text{-}CH)_n- \quad\quad -(CH_2\text{-}CH)_n\text{--}(CH_2\text{-}CH)_n- \quad (4.1)$$

The absorbency of cross-linked polymer can be explained in term 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. The swelling equilibria of ionized hydrogels are determined by a balance of three main forces [69, 70]:

1) the free energy of mixing of the network chains with solvent,

2) the net osmotic pressure within the network, resulting from the mobile counterions surrounding the fixed-charge groups(ion swelling pressure),

3) the elastic retractile response of the network(elastic swelling pressure).

Forces (1) and (2) favor hydrogel swelling, where force (3) opposed it. A classical cross-linked 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.

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 cross-link density. The relationship involving the equilibrium swelling ratio, Q, defined as the ratio of the final swollen volume to the original unswollen volume of the network, was derived by Flory [71]. If the cross-link density is not too high and the solvent is a good solvent, the following approximated relationship was obtained

$$Q^{5/3} = \frac{(1/2 - \chi_1)\, 2\, \overline{M}_c}{V_1 \rho_0 \upsilon_{2,r}^{2/3} (1 - 3\, \overline{M}_c/\overline{M}_n)} \qquad (4.2)$$

Where χ_1 is the polymer-solvent interaction parameter, V_1 is the molar volume of solvent, $\upsilon_{2,r}$ is the polymer volume fraction at cross-linking, $\overline{M}_c$ is the molecular weight of polymer chain between cross-links, and $\overline{M}_n$ is the initial molecular weight of the uncross-linked polymer.

The parameter that describes the basic structure of the hydrogel is the molecular weight between cross-links, $\overline{M}_c$. This parameter defines the average molecular size between two consecutive junctions regardless of the nature of those junctions. Additional parameters of importance in structural analysis of hydrogels are the cross-linking density, ρ_x, which is related to $\overline{M}_c$ as defined by equation (4.3) [11]

$$\rho_x = 1/(\overline{V}\overline{M}_c) \qquad (4.3)$$

Where $\overline{V}$ is the specific volume of the polymer. The determination of cross-link density is described in Appendix C.

From equations 4.2 and 4.3, the equilibrium swelling ratio, Q is inversely-related with the cross-link density, ρ_x.

4.3 Optimum neutralization degree of acrylic acid

The water absorbing capacity of the cross-linked copolymers synthesized with 60:40 molar ratio of AM:KA by 1.4 g/l $(6.14 \times 10^{-3} M)$ $(NH_4)_2S_2O_8$, 1% w/v of organic phase, Span 80 at various neutralization degrees of acrylic acid and cross-linking agent concentrations was shown in Table 4.6 and Figure 4.7.

Table 4.6

Effect of the neutralization degree of acrylic acid at various cross-linking agent concentrations on water absorbency of the synthesized beads.

Neutralization degree	Water absorbency capacity (g/g)		
of acrylic acid	0.025% N,N′-MBA	0.05% N,N′-MBA	0.075% N,N′-MBA
100%	775 ± 99	568 ± 27	476 ± 15
76%	581 ± 18	557 ± 51	471 ± 42
59%	570 ± 68	523 ± 39	428 ± 28
46%	507 ± 59	476 ± 17	447 ± 14

The cross-linked copolymer of potassium acrylate(KA) and acrylamide(AM) gave the optimum result for 100% neutralized poly(acrylic acid) with a water absorbing capacity of 775 g/g at 0.025% mole N,N′-MBA. The water absorbing capacity was decreased with decreasing neutralization degrees of acrylic acid. The low neutralized poly(acrylic acid), having many free, non-neutralized carboxylic, functionalities that cause an auto-cross-linking through a hydrogen abstraction from the polymer backbone, followed by radical combination [1, 67].
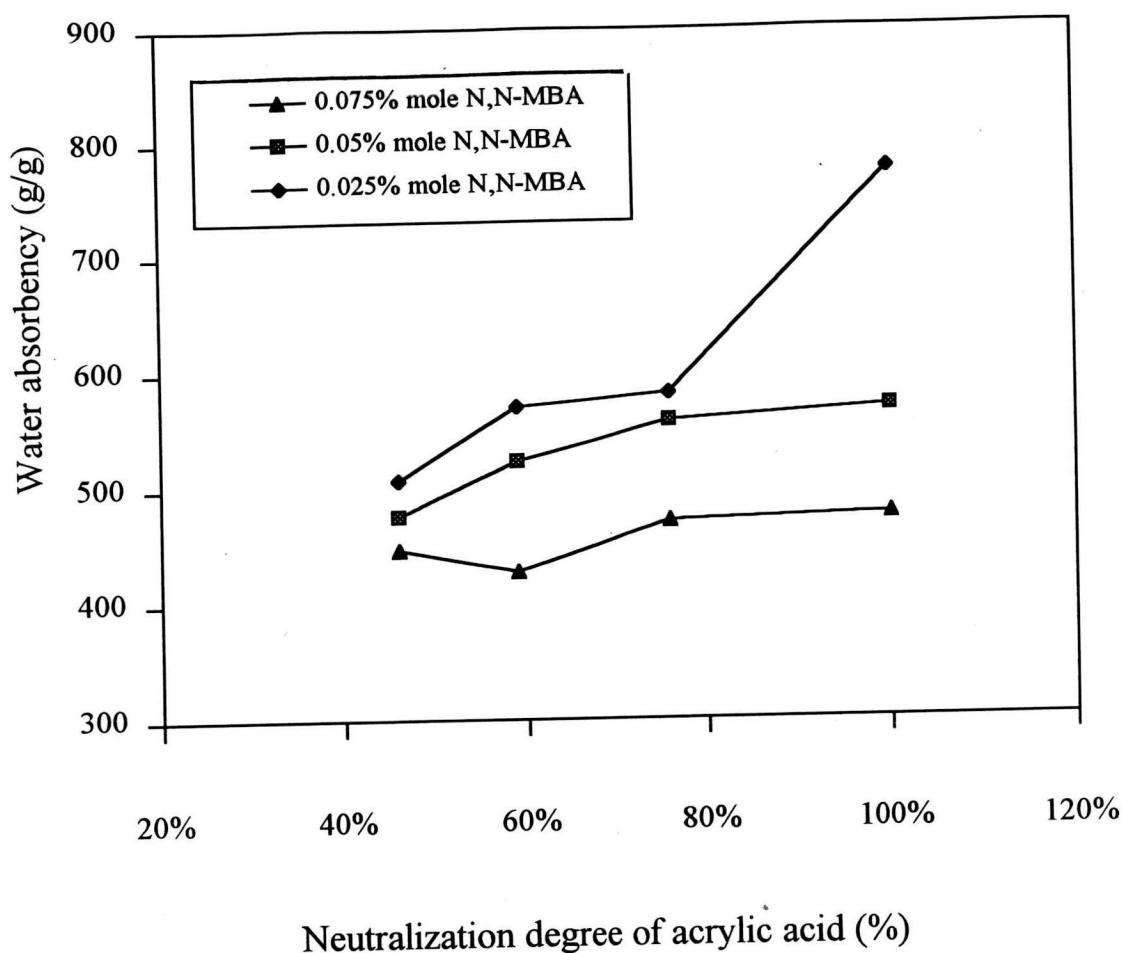
Figure 4.7 Effect of the neutralization degree of acrylic acid at various cross-linking agent concentrations on water absorbency of the synthesized beads.

4.4 Optimum concentration of the initiator

The effect of $(NH_4)_2S_2O_8$ concentration for inverse suspension copolymerization of AM:KA on absorption properties is shown in Table 4.7 and Figure 4.8.

Table 4.7

Effect of the concentration of the initiator on water absorption capacity of

synthesized copolymer beads.

Initiator concentration, g/l, of aqueous phase	% water absorbency (g/g)	Vortex time (sec)
$0.5 \ (2.19 \times 10^{-3} \ M)$	no reaction	-
$1.0 \ (4.39 \times 10^{-3} \ M)$	701 ± 84	32.32 ± 1.66
$1.4 \ (6.14 \times 10^{-3} \ M)$	775 ± 99	21.41 ± 1.05
$1.8 \ (7.89 \times 10^{-3} \ M)$	678 ± 25	19.18 ± 0.62
$2.2 \ (9.65 \times 10^{-3} \ M)$	666 ± 29	19.86 ± 3.32
$2.6 \ (1.14 \times 10^{-2} \ M)$	661 ± 77	23.23 ± 0.23

The copolymers, synthesized by 1.4 g/l(6.14×10^{-3} M) $(NH_4)_2S_2O_8$ gave the optimum result which has the highest water absorbency. Figure 4.8 shows that the water absorbing capacity of the copolymers increased with increasing initiator concentrations to an optimum result at 1.4 g/l(6.14×10^{-3} M) $(NH_4)_2S_2O_8$ and then decreased with increasing initiator concentrations. As shown previously in equation 2.2, the rate of polymerization depended on the concentration of monomers and initiators, for bimolecular termination. The persulphate ions($S_2O_8^{2-}$), aqueous solution, when are heated alone or in the presence of a reducing agent, decomposes to sulphate radical ions(SO_4^{-}). These primary radicals will initiate the monomer to form free radicals of monomer, which propagate monomer molecules in succession to form a large polymeric radical and a dead polymer in the termination step. The rate of polymerization at low concentration of persulphate ions, low quantities of produced free radicals, is slower than high concentration. But at high concentration of persulphate ions,

high quantities of produced free radical may occur chain transfer to polymer [18], so the synthesized copolymer has high cross-link density, which effect to the water absorbency capacity.
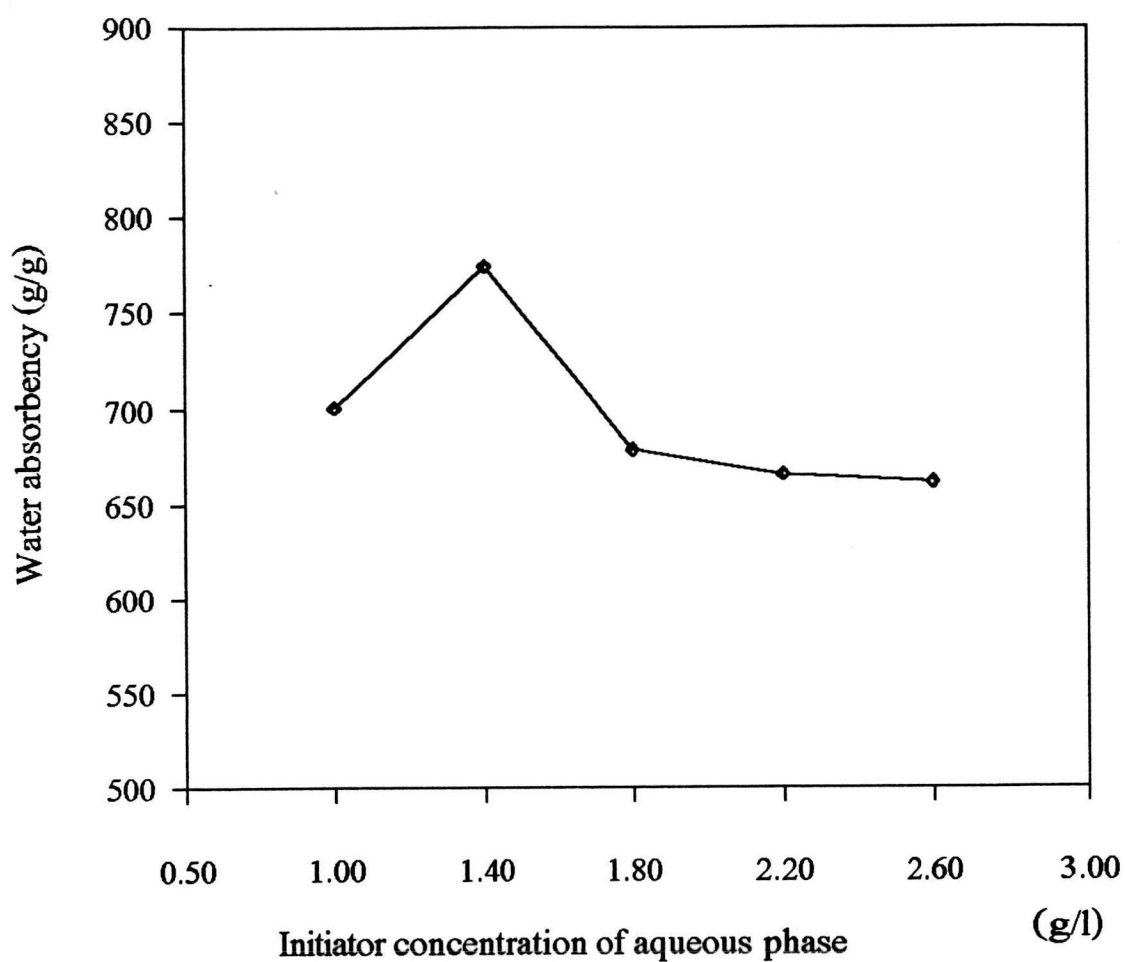

Figure 4.8 Effect of the concentration of the initiator on water absorbing capacity of synthesized copolymer beads.

4.5 The optimum concentration of the suspending agent

The optimum condition for synthesizing the copolymers, described in Section 4.2, which was selected to study other effects on the water absorbency are 60:40 molar ratio of AM:KA, total monomer concentration, 5 M with the cross-linking agent concentration of 0.025% mole of monomer, 1.4 g/l $(6.14 \times 10^{-3}\ M)$ $(NH_4)_2S_2O_8$, and 100% neutralization, of acrylic acid. In this Section, the synthesized copolymers, were produced by the fixed conditions as previously, but with various concentrations of the suspending agent(Span 80) are shown in Table 4.8 and Figure 4.9.

Table 4.8

Effect of the suspending agent concentration on the water absorbency

of the synthesized beads

Suspending agent, Span 80 %w/v of organic phase	% water absorbency (g/g dry polymer)	Vortex time (sec)
0.5	607 $\pm$ 24	33
1.0	775 $\pm$ 99	21
1.5	570 $\pm$ 65	28
2.0	606 $\pm$ 25	27

The optimum suspending agent concentration was 1.0% w/v of the organic phase to give the copolymer which has the highest water absorbency($\cong$775). The results given in Table 4.8 show that the water absorbing capacity of copolymer beads is dependent on the concentration of suspending agent. Two effects may

be responsible for these results [66]: (1) The levels of grafting reaction of the suspending agents onto the particle surface; and (2) the particle size. If the suspending agent was grafted onto the particle surface, then the hydrophobic polymeric layer might retard water penetration and reduce the water absorbing capacity.
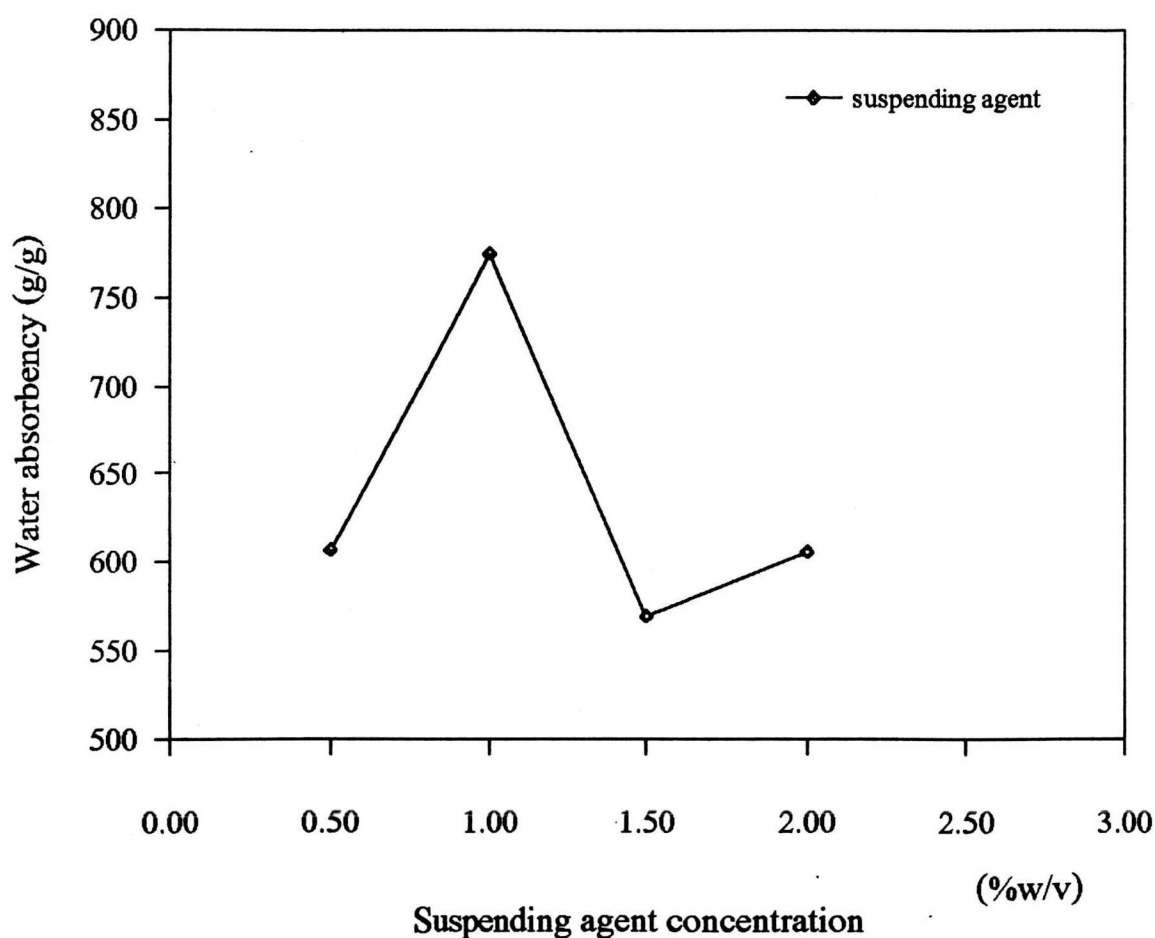

Figure 4.9   Effect of the suspending agent concentration on the water absorbency of the synthesized beads.

4.6 Type of the suspending agent

The water absorbency of the copolymer beads, synthesized by 60:40 molar ratio of AM:KA with 1.4 g/l(6.14×10^{-3} M) $(NH_4)_2S_2O_8$, 1% w/v suspending agent, and 0.025 %mole N,N$'$-MBA at various types of the suspending agent was shown in Table 4.9 and Figure 4.10.

Table 4.9

Effect of type of the suspending agent on water absorbency

Type of suspending agent	Surface tension in n-hexane (mN/m) at 27°C	%Water absorbency (g/g)	Vortex time (sec)
Span 40	45	664 $\pm$ 40	20.34
Span 60	34	688 $\pm$ 52	27.02
Span 80	31	775 $\pm$ 99	21.41

The synthesized beads gave the optimum product properties for Span 80 surfactant as suspending agent with a water absorbency value of 775 g/g.

The type and concentration of the suspending agent affect the particle size of synthesized copolymer beads [66]. While the Hydrophilic-Lipophilic balance (HLB) number of acrylamide/salt acrylate monomer mixtures were between 9 and 10, the HLB numbers of the suspending agent (Span series), which resulted in successful inverse suspension polymerization recipes, were in the range between 4 and 7. They are Span 80(sorbitan monooleate), Span 60(sorbitan monostearate), and Span 40(sorbitan monopalmitate) with the HLB values of 4.3, 4.7, and 6.7, respectively.

When different suspending agents were used in the inverse suspension polymerization, the particle size of the suspending beads varied with their stabilization efficiency as shown in Figures 4.10- 4.12. The average particle size distribution was increased with increasing HLB values, which related to the decreasing water absorbency capacity of synthesized copolymer beads, i.e., Span 40(133 μm) > Span 60(101 μm) > Span 80(76 μm). This result is in contrast with the fact that the particles size of the suspending beads depend on their stabilization efficiency, from which the size increases with decreasing HLB numbers due to decreasing stabilization efficiency. The effects, which may be responsible for this result, if it was considered with the chemical, physical properties and surface tension in n-hexane of suspending agents as shown in Tables 4.9 and 4.10.
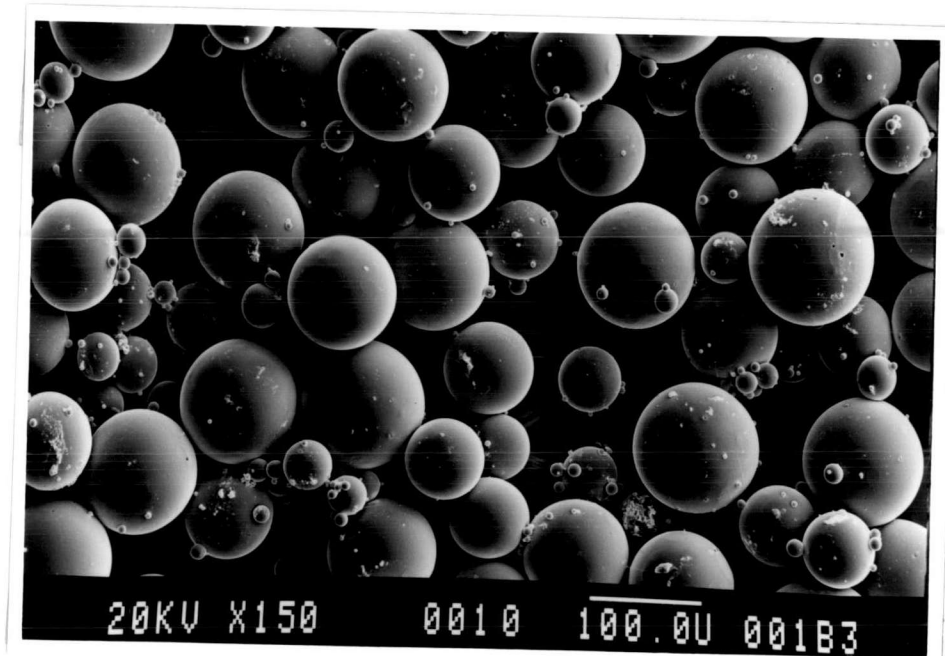
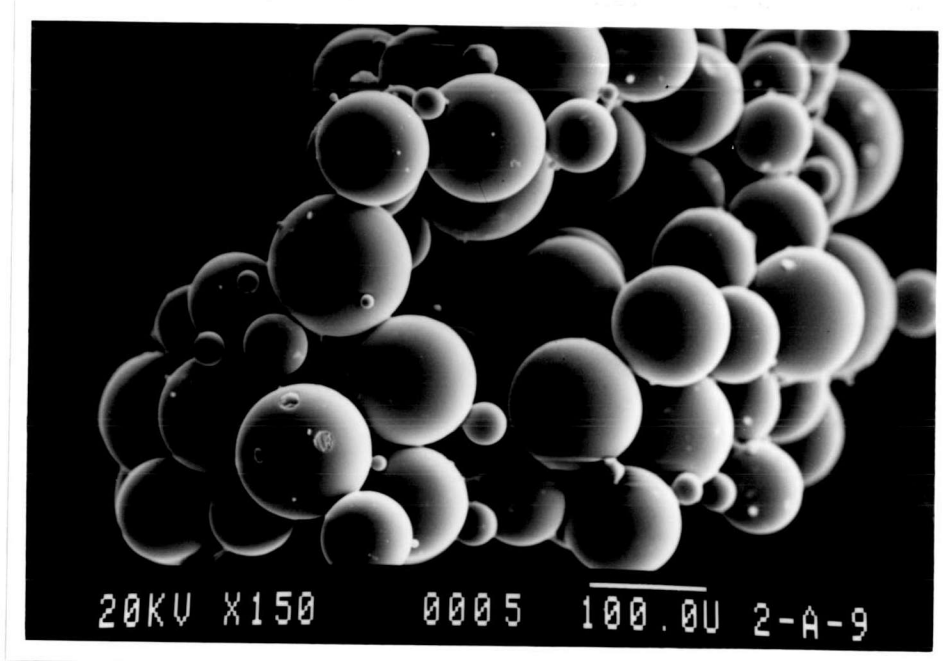Figure 4.10 SEM of copolymer beads, synthesized by Span 80

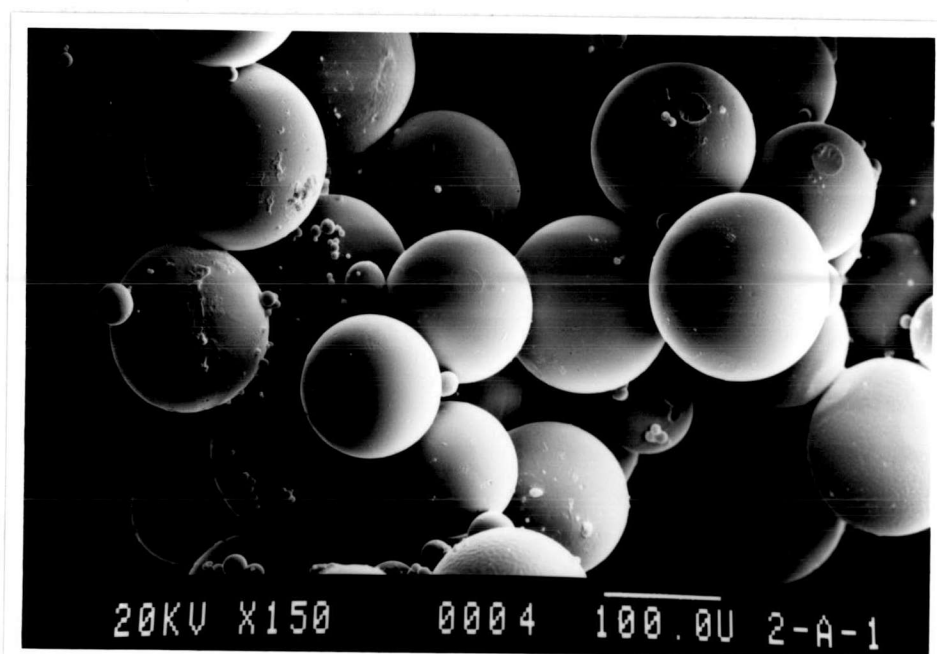Figure 4.11 SEM of copolymer beads, synthesized by Span 60

Figure 4.12 SEM of copolymer beads, synthesized by Span 40

Table 4.10

The chemical and physical properties of suspending agents

Product name	Chemical name	Acid values*	Sponification value*	Hydroxyl value	HLB	Solubility (10% sol., 25°C)			
						water	ethanol	N-hexane	xylene
Span 40	Sorbitan monopalmitate	7.5 max	140-150	275-305	6.7	H	D	H	S
Span 60	Sorbitan monostearate	5-10	147-157	235-260	4.7	H	D	H	S
Span 80	Sorbitan monooleate	5.5-7.5	149-160	193-209	4.3	I	S	S	S

Solubility : S; Totally soluble, H; Hazy, I; Insoluble, D; Slightly soluble

* Unit = milligram of KOH that just right react with gram of sample

From Table 4.10, Span 40 has the highest hydroxyl value, then it might be effective to the level of grafting of the suspending agent onto the particle surface, the hydrophobic polymeric layer could retard water penetration [66]. In addition, the solubility in n-Hexane of Span 80 is better than those of Span 40 and Span 60, that confirmed by the measured surface tension value of those, which are 31, 45, and 34 mN/m at 27°C, respectively. So the suspension droplet size of Span 80 as suspending agent is smaller than others that gives more surface area, resulting in the high water absorbency capacity.

4.7 Buffer effect on swelling behavior

The influence of solution pH(2-12) on water absorption capacity of the synthesized copolymers, produced by inverse suspension polymerization of total monomer concentration, 5 M, at various molar ratios of AM:KA with 0.025% N,N$'$-MBA, 1% w/v Span 80, 1.4 g/l($6.14\times10^{-3}M$) $(NH_4)_2S_2O_8$ and 100% neutralization degree of acrylic acid in a sodium salt of citrate-phosphate-borate buffer solution system alters the water absorbency as shown in Table 4.11 and Figure 4.13.

The swelling capacity of the copolymer beads are very dependent on pH, and composition of the absorbed liquid. Figure 4.13 shows that the absorbency of synthesized copolymer beads, of various molar ratios of AM:KA reaches a maximum at pH 5. The swelling of copolymer beads was found to increase significantly from pH 2 to pH 5, and remain relatively constant afterwards.

Table 4.11

Effect of pH on swelling behavior of copolymer beads at 25°C

Molar ratio AM:KA	% Water absorbency (g/g)							in distilled water
	at various pH of buffer solution							
	pH 2	pH 3	pH 5	pH 7	pH 9	pH 11	pH 12	
10:90	14	35	59	62	61	61	62	582
30:70	11	25	72	75	70	65	69	575
50:50	9	20	63	63	59	61	65	525
60:40	4	14	59	59	55	58	56	775
80:20	25	26	53	55	50	48	50	629
90:10	27	23	35	38	35	34	38	456

Normally, hydrogels are also classified into three categories by their ionic character [56]. In particular, anionic hydrogels prepared by the copolymerzation of acrylic acid are important for industrial products that are used widely as superabsorbent hydrogels. Cationic ones, however, have not been much developed as industrial products. Nonionic ones are very useful, since they can absorb water in a wide range of pH and there is no ionic interaction between the solutes in water and gel matrix.

Sodium cation in citrate-phosphate-borate buffer can interact with anions on the network, thus decreasing the charge density of anions on the network that retard the ion exchange between H^+ ions from inside and outside the gel network. This result is far lower than the water absorbency of copolymer in distilled water, because of the ionic contents.
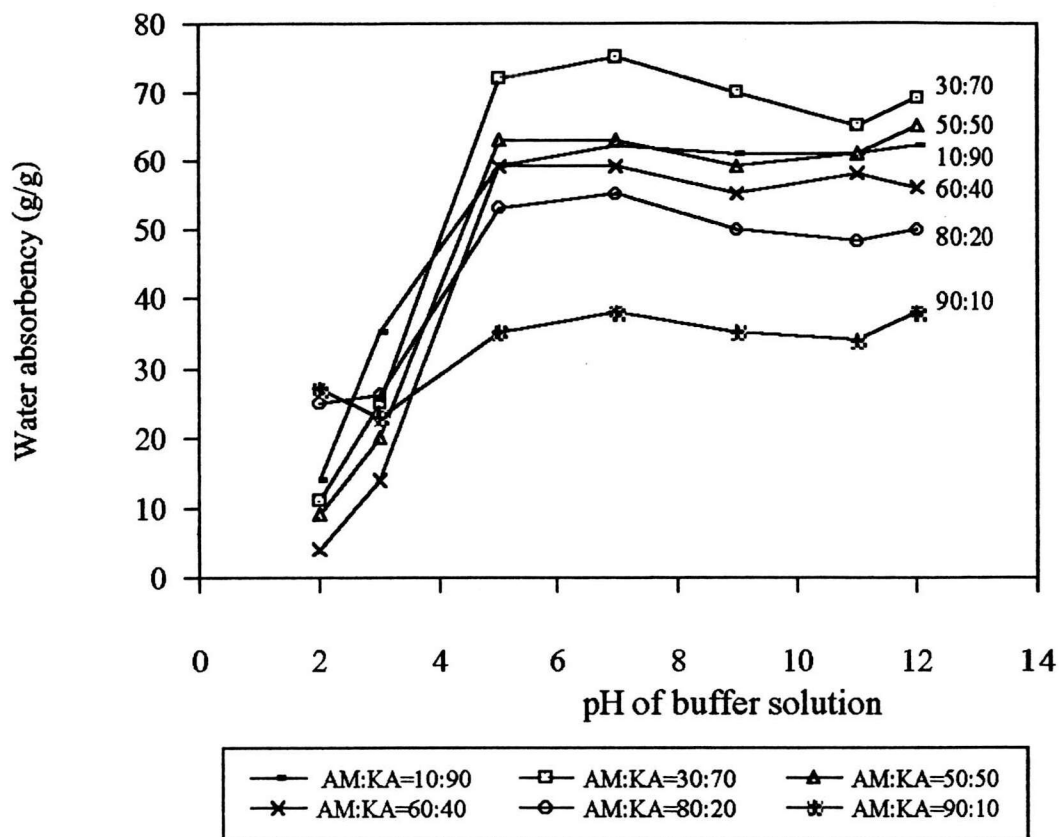
Figure 4.13 Effect of pH on swelling behavior of copolymer beads at 25°C

For theoretical framework developed to describe the equilibrium swelling characteristic of net works were Flory-Rehner model, Peppas-Merrill model, and Peppas-Luchy model [72]. The developed model for anionic polymeric network interacting cross-linked with solvents present and exhibiting a non-Gaussian chain length distribution, the complete equilibrium expression is shown equation (4.4):

$$\frac{V_1}{4I}\left[\frac{\upsilon_{2,s}}{\overline{\upsilon}}\right]^2 \left[\frac{K_a}{10^{pH}+K_a}\right]^2 = \left[\ln(1-\upsilon_{2,s}) + \upsilon_{2,s} + \chi_1 \upsilon_{2,s}^2\right]$$

$$+ \frac{\left[\frac{V_1}{\overline{\upsilon}\,\overline{M}_c}\right]\left[1 - \frac{2\overline{M}_c}{\overline{M}_n}\right]\upsilon_{2,r}\left[\left[\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right]^{1/3} - \frac{1}{2}\left[\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right]\right]\left[1 + \frac{1}{N}\left[\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right]^{1/3}\right]^2}{\left[1 - \frac{1}{N}\upsilon_{2,s}^{2/3}\right]^3} \qquad (4.4)$$

Where

V_1 = the molar volume of the swelling agent

I = ionic strength

$V_{2,s}$ = the polymer volume fraction in the equilibrium-swollen polymer

$V_{2,r}$ = the polymer volume fraction in the sol-called relaxed polymer state

χ_1 = the Flory polymer-solvent interaction parameter

N = the effective number of bond vectors between consecutive crosslinks

$\overline{M}_n$ = the number average molecular weight before cross-linking

$\overline{M}_c$ = the number average molecular weight between crosslink-linking

$\overline{V}$ = the specific volume of the polymer.

Based on equation 4.4, the molar volume of the swelling agent is increased with increasing pHs of the solution.

As shown previously in, Section 4.2, the swelling equilibria of ionized hydrogels are determined by a balance of three primary forces. The main forces that favor hydrogel swelling are the free energy of mixing of the network chains with solvents and the ionic osmotic pressure generated from mobile counterions to charged ions in the net work(Donnan equilibrium) [73]. For this result, it is the latter force is plausible explained as follows:

The simplest of the theories attributes the ion swelling pressure to the difference between the osmotic pressure of freely ions in the gel and the outer solution, the distribution of the ions between the gel and the outer solution forms Donnan equilibrium. Within this theory, the ionic forces depend only on the ionic composition of the solvent and on the concentration of fixed ionizable group in the gel but not on the properties of the neutral network [73].

The external pH has a profound effect on the balance of forces that determine equilibrium swelling in these gels. The molar ratio of AM:KA in hydrogel, which will give the optimum swelling, should be 90:10. As the pH is lowered to the strong acidic region, the amide side chains of the acrylamide become hydrolyzed to be the carboxylic group, thus decreasing the charge density of anions on the network. The concomitant decreases in mobile counter-ion content of the network sharply decreases the internal osmotic pressure which retards the observed swelling transitions.

The opposite behavior occurs in the weak acid and basic solutions in the pH range 5-12. As increasing the pH, the concentration of the base cations in the outer solution and the concentration of the base anion inside of network will also increase. Those cations will be attracted into the gel to balance the osmotic pressure occurred from the anion of base-hydrolyzed acrylamide and carboxylate group. Those cations will replace the mobile H^+ ions. The gel, of course, acts as an ion exchanger. New H^+ ions will be supplied by water. The concentration of mobile ions in the gel will thus increase more rapidly than in the outer solution, and the ion swelling pressure will increase.

4.8 Swelling behavior in salt solution

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 [74]. The water intake by the gel reduced the osmotic pressure until an ion concentration equilibrium was reached.

The highest water-absorbing copolymer obtained earlier with water absorbency = 775 g/g was selected to test the salt effect in various concentrations of NaCl, KCl, KI, KBr, $MgCl_2$, and $CaCl_2$ solutions. The influences of salt solutions upon water absorbency of the copolymer are summarized in Table 4.12 and Figure 4.14.

Table 4.12

Effect of different salt solution concentrations on water absorbency of the copolymer.

Concentration of salt solution (%w/v)	Water absorbency (g H_2O/g dry polymer)					
	NaCl	KCl	KI	KBr	$MgCl_2$	$CaCl_2$
0.000	775 ± 99	775 ± 99	775 ± 99	775 ± 99	775 ± 99	775 ± 99
0.005	570 ± 20	551 ± 42	562 ± 20	548 ± 34	547 ± 13	477 ± 12
0.05	212 ± 7	244 ± 10	334 ± 17	299 ± 22	109 ± 0.7	87 ± 11
0.1	154 ± 5	178 ± 5	244 ± 5	208 ± 3	80 ± 2	52 ± 3
0.3	93 ± 4	109 ± 4	154 ± 4	132 ± 0.4	37 ± 1	22 ± 1
0.5	75 ± 0.6	87 ± 2	123 ± 2	105 ± 3	25 ± 2	16 ± 1
0.9	60 ± 0.2	68 ± 0.9	98 ± 0.9	81 ± 2	19 ± 1	12 ± 1

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 surrounding the polymer. An addition of a simple salt to the polymer solution leads to network contraction as indicated by viscosity lowering and the decreasingly chemical potential of the water surrounding a polyelectrolyte polymer. Therefore, absorbent polyelectrolyte polymers cannot imbile as much salt water as pure water [71].
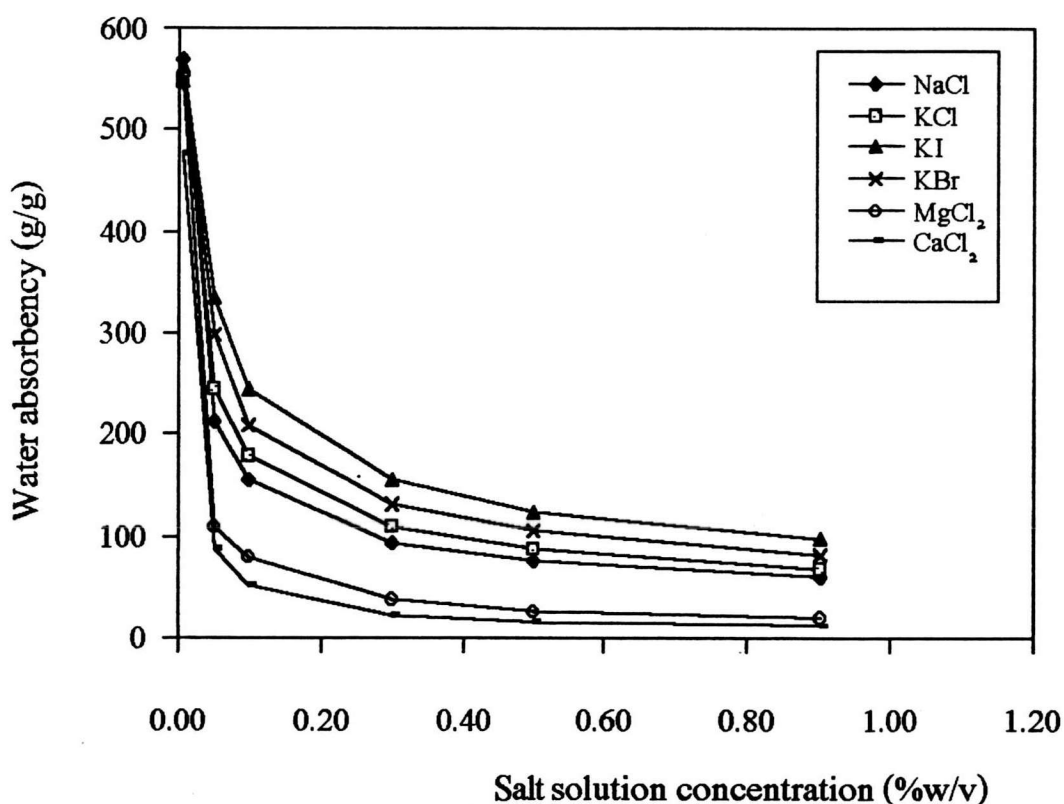
Figure 4.14 Effect of different salt solution concentrations on water absorbency of the copolymer.

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. At low ionic strength(large Debye lengths), repulsions are long-range interaction and the gel expansion to minimize the repulsion free energy; as ionic strength rises(small Debye lengths), repulsions are shielded and the gel dewash [75]. The ion concentration and ionic strength of the salt solutions are calculated in Table 4.13.

On observing the case of $MgCl_2$ and $CaCl_2$, the water absorbency decreases even more with increasing $MgCl_2$ and $CaCl_2$ 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 $MgCl_2$ and $CaCl_2$ solutions comparing with that of other salt solutions at the same concentration or, less divalent than monovalent cations are needed to maintain the charge balance, the drop will occur at lower salt concentrations in the divalent case. In addition, the divalent Mg^{2+} and Ca^{2+} ions may cross-link the gel by salt formation with the carboxylate groups on adjacent chains or chain segments of the copolymer. Consequently, the cross-link density of the network increases [74, 77, 78].

At the same ionic strength value, the water absorbency of copolymers in various salt solutions containing different cations and anions are shown in Figures 4.15-4.16. The water absorbency of copolymers is relatively equal, except for the results of $MgCl_2$ and $CaCl_2$ solutions, the divalent salts differ because Mg^{2+} and Ca^{2+} can react with the free carboxylic sites of the gel by a chelate formation to give additionally divalent carboxylate groups on the backbone.
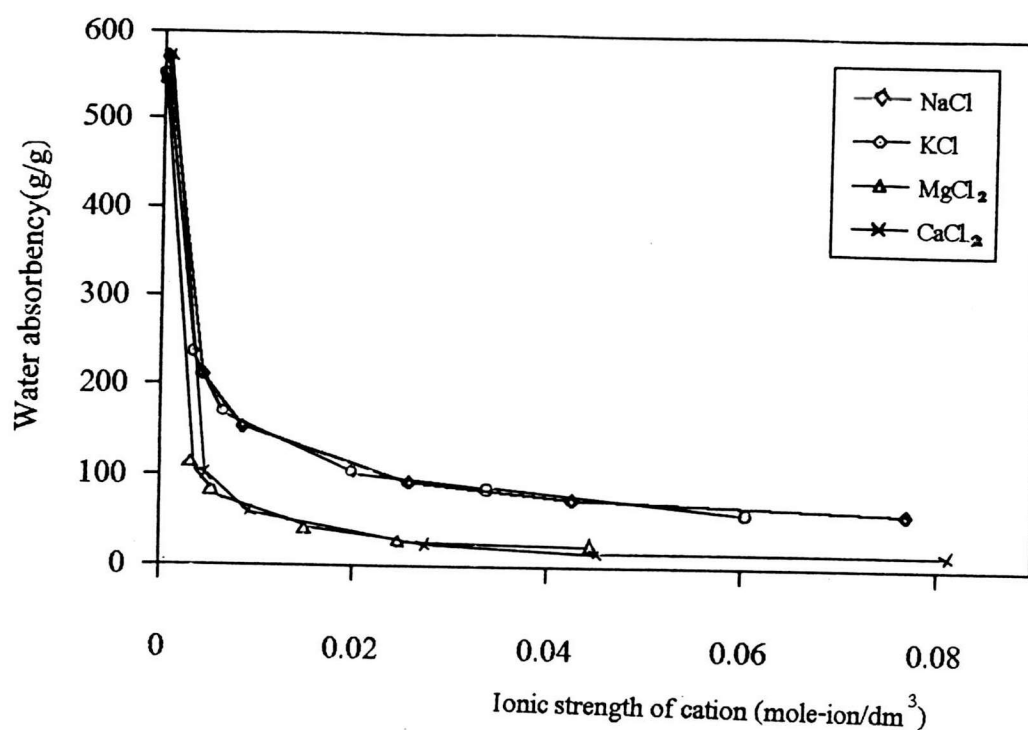
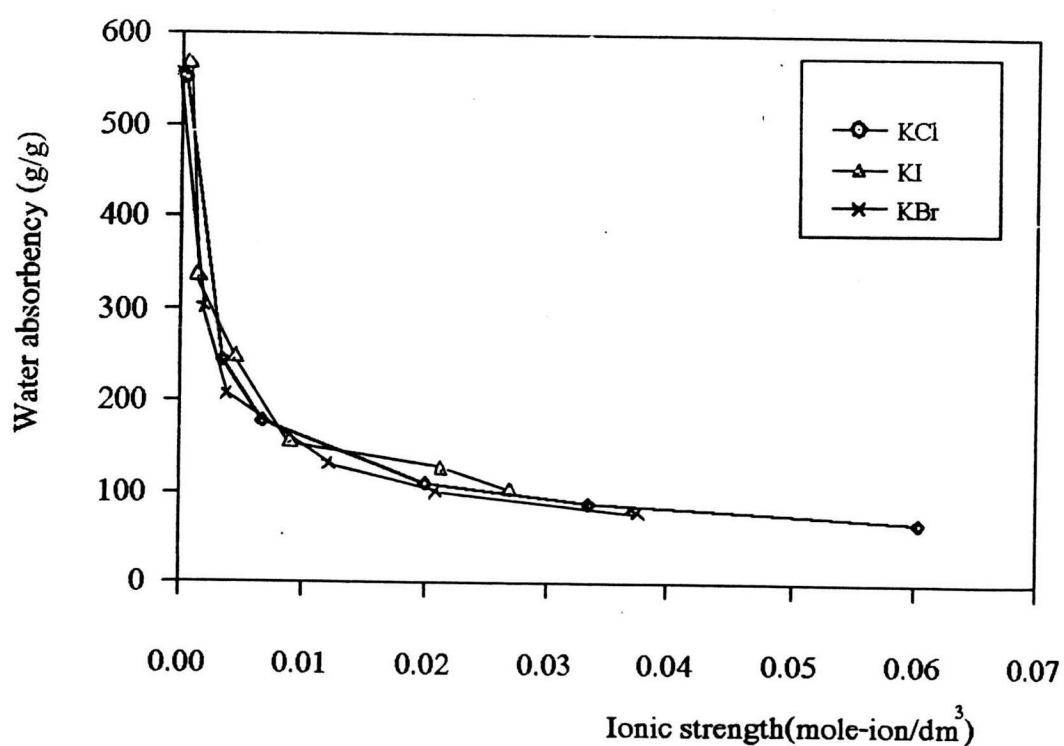Figure 4.15 Effect of cation in series of salt of chloride on water absorbency of the copolymer.

Figure 4.16 Effect of anion of salt solution on water absorbency of the copolymer.

Table 4.13

ionic strength of the salt solutions

Concentration of salt solution (%wt/v)	Ionic strength of salt solutions* (mole-ion/dm^3)					
	NaCl	KCl	KI	KBr	MgCl$_2$	CaCl$_2$
0.005	8.5558×10^{-4}	6.7060×10^{-4}	3.0119×10^{-4}	4.2017×10^{-4}	7.3779×10^{-4}	1.3515×10^{-3}
0.05	8.5558×10^{-3}	6.7060×10^{-3}	3.0119×10^{-3}	4.2017×10^{-3}	7.3779×10^{-3}	0.01351
0.1	0.0171	0.0134	8.6199×10^{-3}	8.4034×10^{-3}	0.0148	0.0270
0.3	0.0513	0.0402	0.0181	0.0252	0.0443	0.1811
0.5	0.0856	0.0671	0.0431	0.0420	0.0738	0.1351
0.9	0.1540	0.1207	0.0542	0.0756	0.1329	0.2433

*$I = \frac{1}{2} \sum (C_i Z_i^2)$; where I, C_i and Z_i are the ionic strength, the ionic concentration and charge on each individual ion, respectively [76].

4.9 The rheological properties of the copolymers

The viscosimetric properties of the synthesized copolymers, produced by inverse suspension polymerization of total monomer concentration, $5\ M$, at 60:40 molar ratio of AM:KA, with various cross-linking agent concentrations, N,N'-MBA, 1% w/v Span 80, 1.4 g/l($6.14 \times 10^{-3}\ M$) and 100% neutralization degree of acrylic acid were shown in Table 4.14 and Figures 4.17-4.19.

Table 4.14

The rheological properties of the copolymers

Cross-linking agent (% mole of monomer)	Water absorbency(g/g)	Viscosity[a] (Pa.s)	Shear stress[b] (Pa)	Shear strain	Shear modulus[c] (Pa)
None	1484 ± 408	0.25	0.5	1200	4.167×10^{-4}
0.025%	775 ± 99	5.5	11	1200	9.167×10^{-3}
0.050%	568 ± 27	6.25	12.5	1200	1.040×10^{-2}
0.075%	519 ± 32	7.75	15.5	1200	1.290×10^{-2}

[a] was calculated from (N x 2.5 x 1000) / 1000 Pa.s, when N is measured value from viscometer.

[b] was calculated from equation Appendix B-7.

[c] was calculated from equation Appendix B-3.

The result shows that the water absorbency of copolymers decreases with increasing shear modulus of the swollen gel, because the increasing cross-linking agent concentration controls cross-link density on net work of the synthesized copolymer, in addition, it increases the elastic retractile response of the network. The water absorbency of swollen gel decreases with the increasing shear modulus

and appears to be constant when increasing the shear modulus of swollen gel. From Figure 4.19, the viscosity of swollen gels, synthesized with various cross-linking agent concentrations decrease with the increasing shear rate and becomes constant when increasing shear rates because of a thinning effect of material [79]. The thinning effect is the influence that materials are thinning due to increasing shear rates. The materials, which have this behavior are called Pseudoplastic materials. With increasing shear rates matchstick-like particles suspended in the liquid will be turned lengthwise into the direction of the flow. Chain-type molecules in a melt or in a solution can disentangle, stretch, and orient parallel to the driving force. Particles or molecular alignments allow particles and molecules to slip past each other more easily in non-crosslinked polymers or low cross-linking density network and this shows up as reduced viscosity.
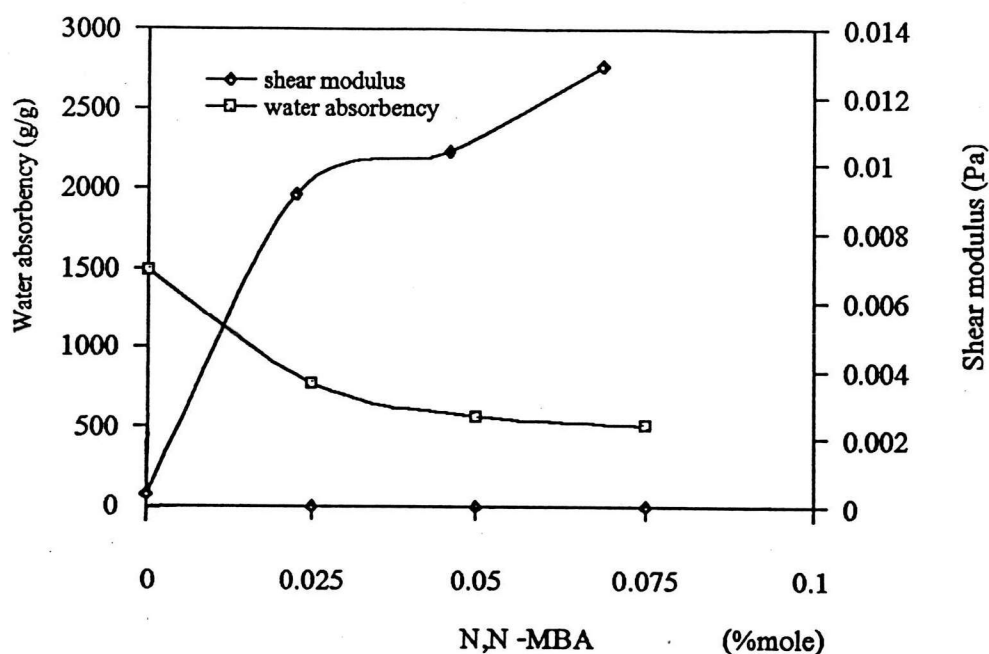
Figure 4.17 The relationship between shear modulus and water absorbency of the synthesized copolymeres, at various cross-linking agent concentrations.

Table 4.15

Effect of shear rates on viscosity and the relationship between shear rates and shear stress of the copolymers, synthesized with various cross-linking agent concentrations.

Shear rates (s^{-1})	0.0% N,N'-MBA		0.025% N,N'-MBA		0.05% N,N'-MBA		0.075% N,N'-MBA	
	Viscosity (Pa.s)	Shear stress (Pa)	Viscosity (Pa.s)	Shear stress (Pa)	Viscosity (Pa.s)	Shear stress (Pa)	Viscosity (Pa.s)	Shear stress (Pa)
1	0.50	0.50	9.50	9.50	10.50	10.50	11.00	11.00
2	0.25	0.50	5.50	11.00	6.25	12.50	7.75	15.50
4	0.313	1.252	3.00	12.00	3.75	15.00	4.13	16.52
8	0.313	2.504	1.81	14.48	2.13	17.04	2.50	20.00
20	0.188	3.76	0.95	19.00	1.03	20.60	1.13	22.60
40	0.156	6.24	0.575	23.00	0.625	25.00	0.50	20.00
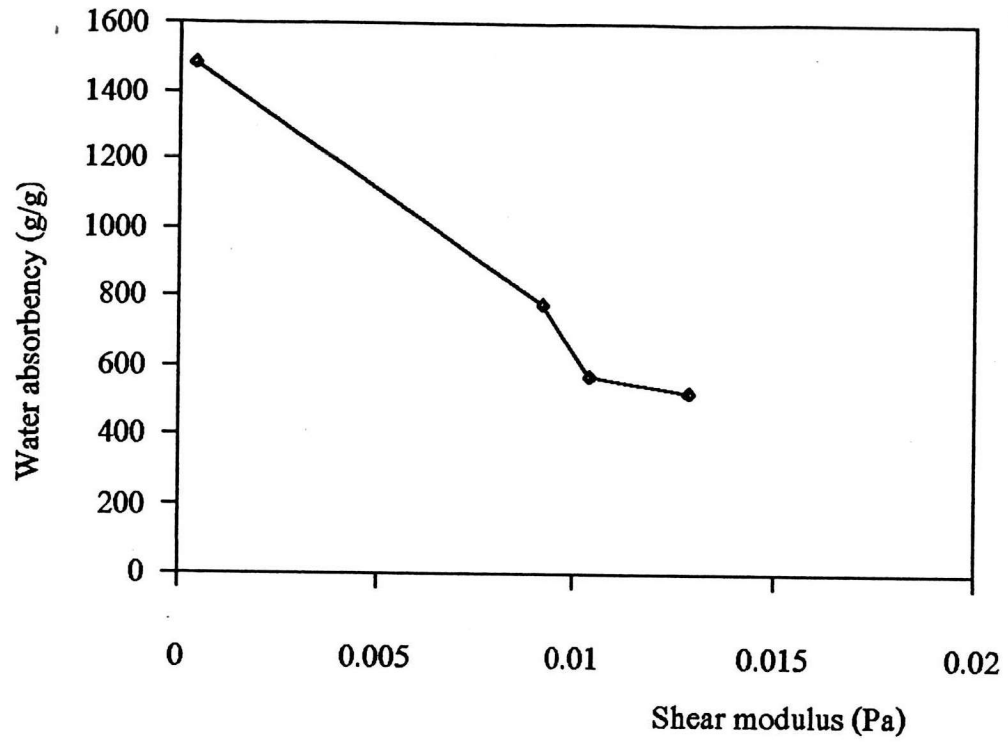
Figure 4.18 Effect of shear modulus on water absorbency of the

synthesized copolymers
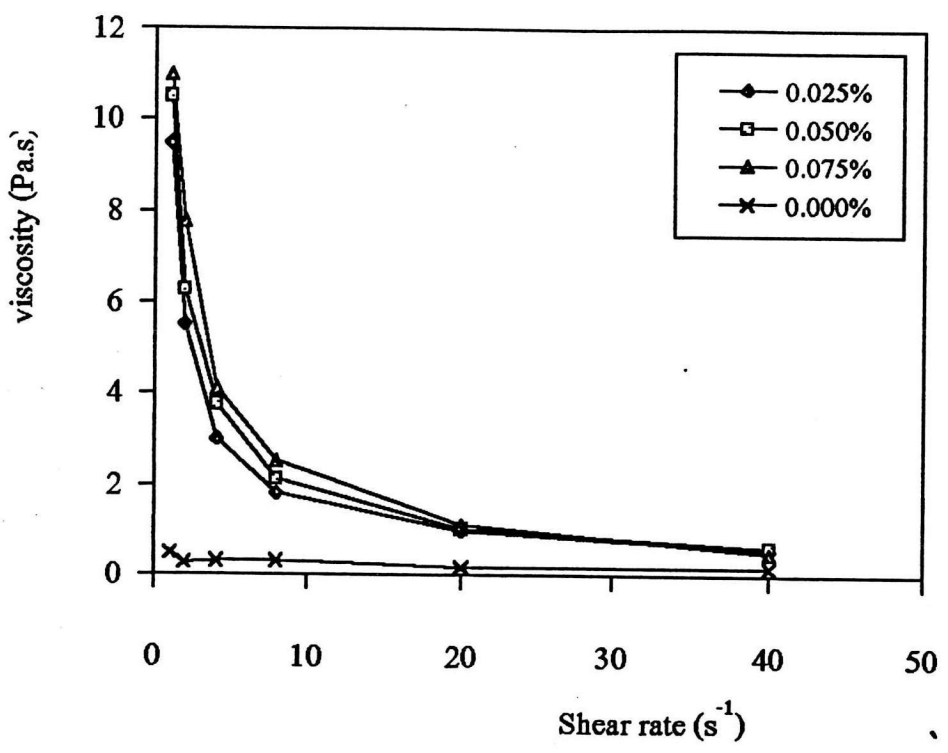
Figure 4.19 Effect of shear rates on viscosity of the synthesized
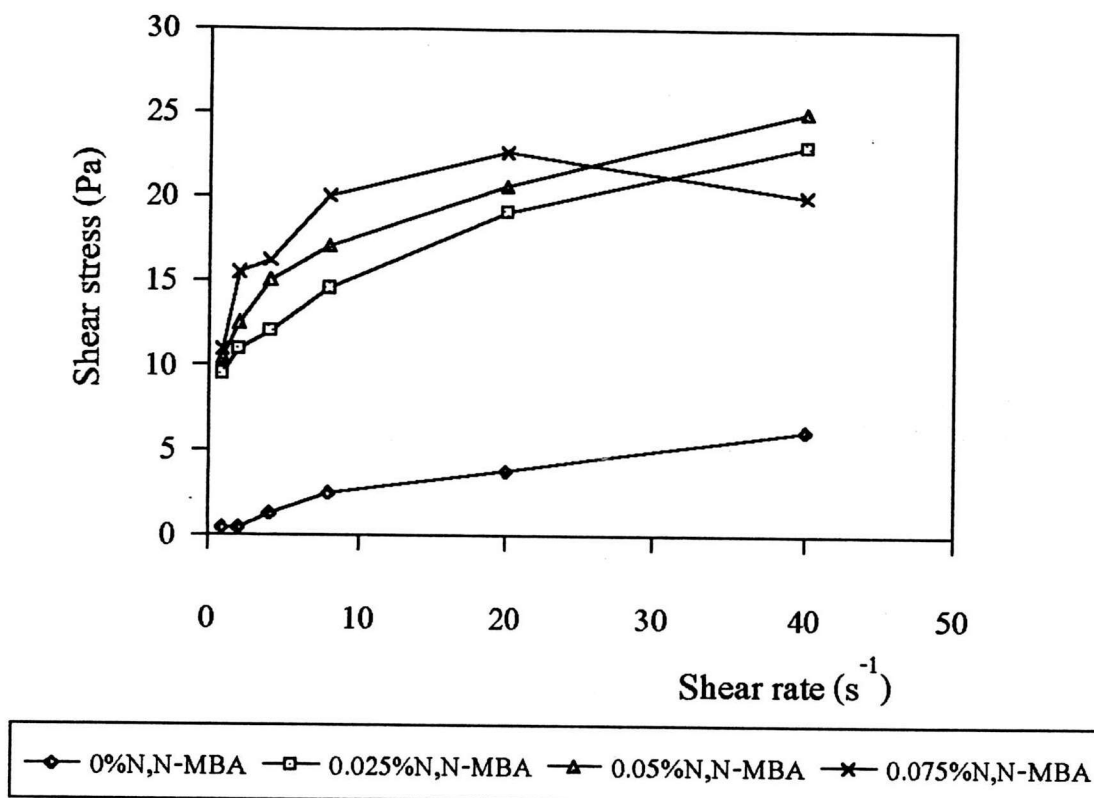
copolymers

Figure 4.20 The relationship between shear rates and shear stress of the synthesized copolymers.

4.10 Characterization

4.10.1 Thermal properties of the copolymer

The copolymers were investigated by DSC to identify T_g and T_m of the copolymer. The DSC thermograms of the copolymers, synthesized with Span 80, Span 60, and Span 40 as suspending agent were shown in Figure 4.21. All DSC thermograms of the copolymers show two endothermic peaks. As such, the phase separation is anticipated to exist in the copolymers. The T_{g1}, T_{m1}, T_{g2}, and T_{m2} of the copolymers are depicted in Table 4.16.

Table 4.16

The T_g and T_m of the copolymers, synthesized with different suspending agent

Suspending agent	Thermal properties ($^\circ$C)			
	T_{g1}	T_{m1}	T_{g2}	T_{m2}
Span 40	89.77	121.67	241.09	256.67
Span 60	97.59	140.00	241.59	255.00
Span 80	101.86	140.00	244.61	260.00

The T_{g1} and T_{g2} are characterized as the T_g of polyacrylamide and poly(potassium acrylate), respectively, whereas the reference T_g values are 165°C and 194°C, respectively [64, 65]. As in Table 4.15, the T_{g1} and T_{m1} of the copolymers, synthesized with different types of suspending agent are different, while T_{g2} and T_{m2} of these copolymers are approximately equal. Thus, the type of suspending agents are essential to the thermal properties of the copolymers, especially at T_{g1} and T_{m1}. The T_{g1} of the copolymer, synthesized with Span 80 as suspending agent is higher than those with Span 60 and Span 40, respectively, which are far lower than the reference T_g value of the polyacrylamide(165°C), while the T_{g2} of all copolymers are far higher than the reference T_g value of poly(potassium acrylate)(194°C). They are probably due to the interference coating of the suspending agent on the surface of the copolymer beads, imidization reaction of acrylamide units and the steric hindrance of the suspending agent molecules.

In addition, the thermal properties of the copolymers depend on the quantity of cross-linking agent as shown in Figure 4.22.
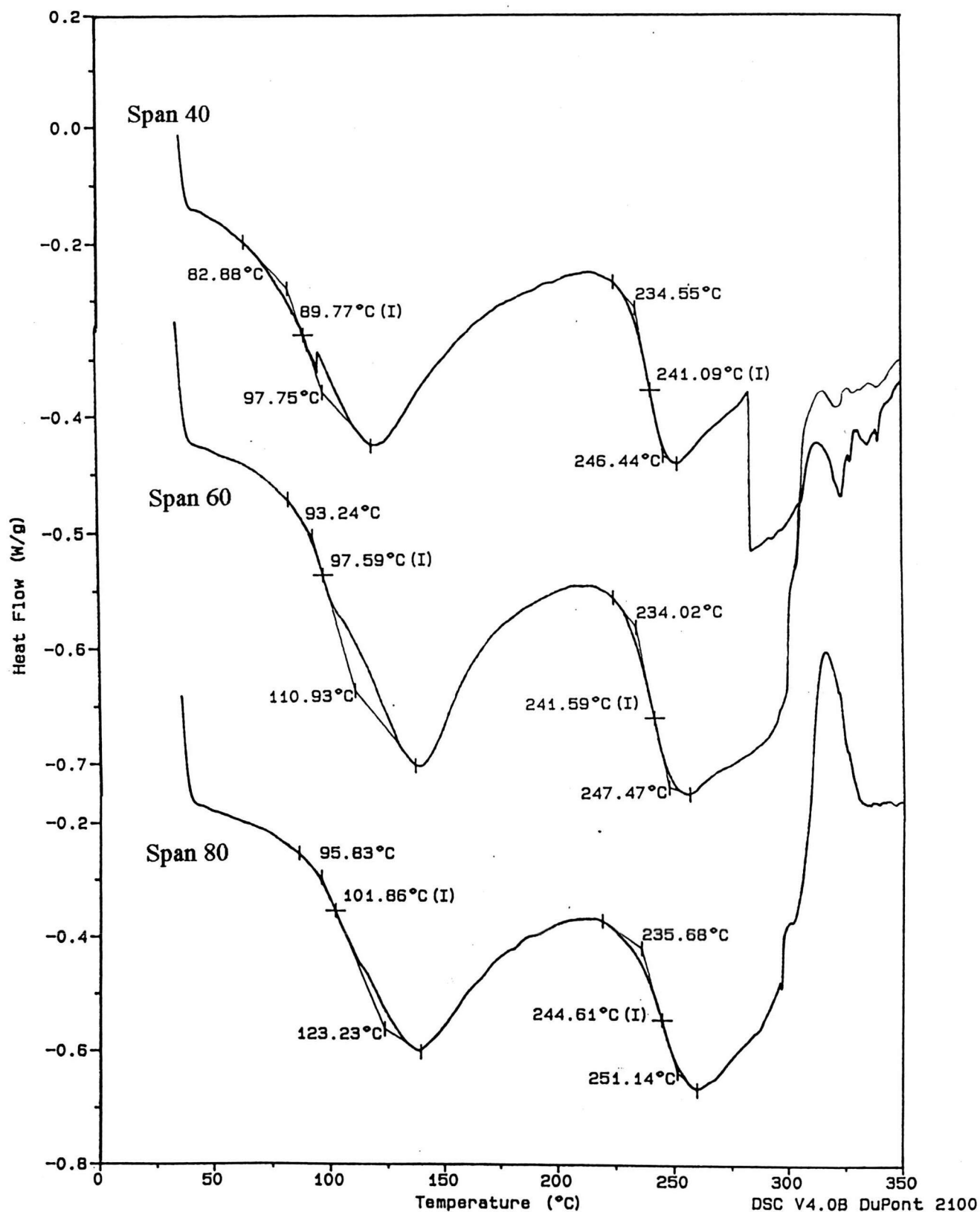
Figure 4.21 DSC Thermogram of the copolymers, synthesized with
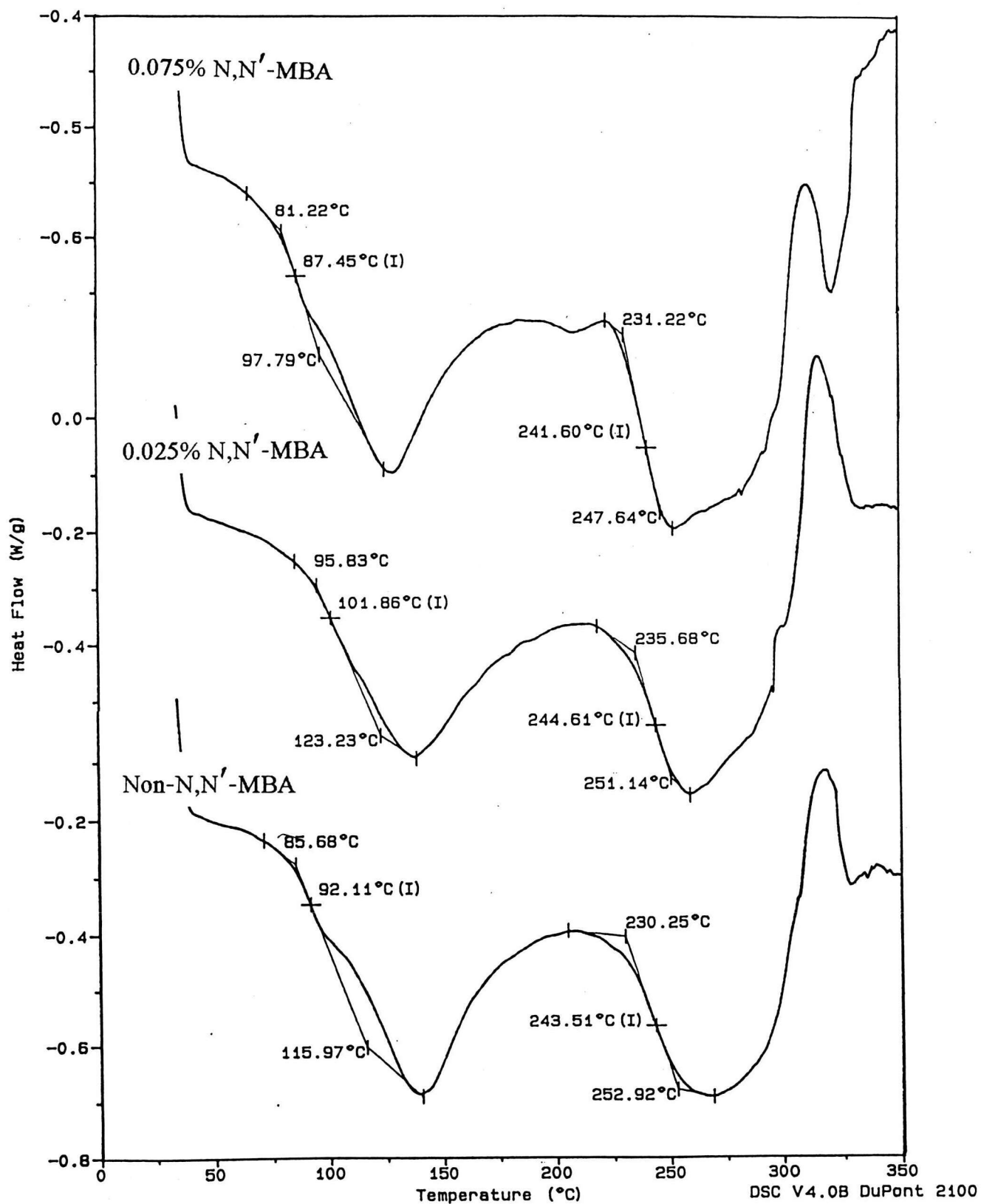
various types of Span, and 0.025% N,N′-MBA

Figure 4.22 DSC Thermogram of the copolymers, synthesized with

various cross-linking concentrations, and Span 80

4.10.2 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 cross-linked copolymers, with different quantities of the cross-linking agent are shown in Figures 4.23-4.26. From the SEM micrographs, lumps are observed on the water-soluble copolymer in Figure 4.23 whereas the cross-linked copolymer beads are rather round in appearance. The cellular structure found in the cross-linked copolymer is shown in Figures 4.27-4.29. The occurrence of the cellular structure may be due to the high molar ratio of acrylamide and high pH used in polymerization to produce polyacrylamide and polyimide networks due to imidization(Figures 4.27-4.29). This structure is may to increase the surface area of the copolymer beads, a requirement for high water absorbency.

20KU X330   0001   100.0U NA-I
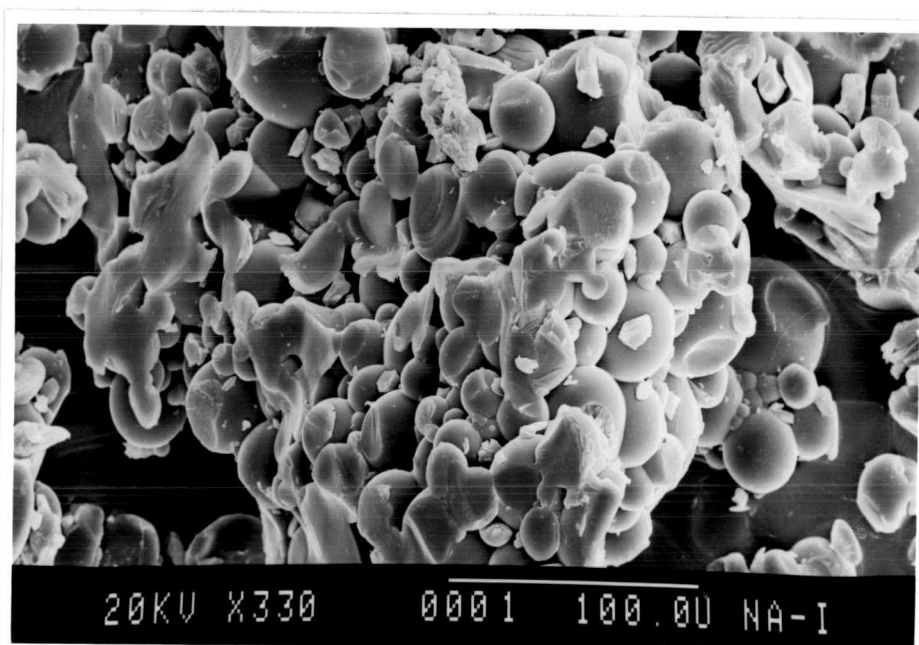
Figure 4.23 SEM micrograph of the water-soluble copolymer, without cross-linking agent
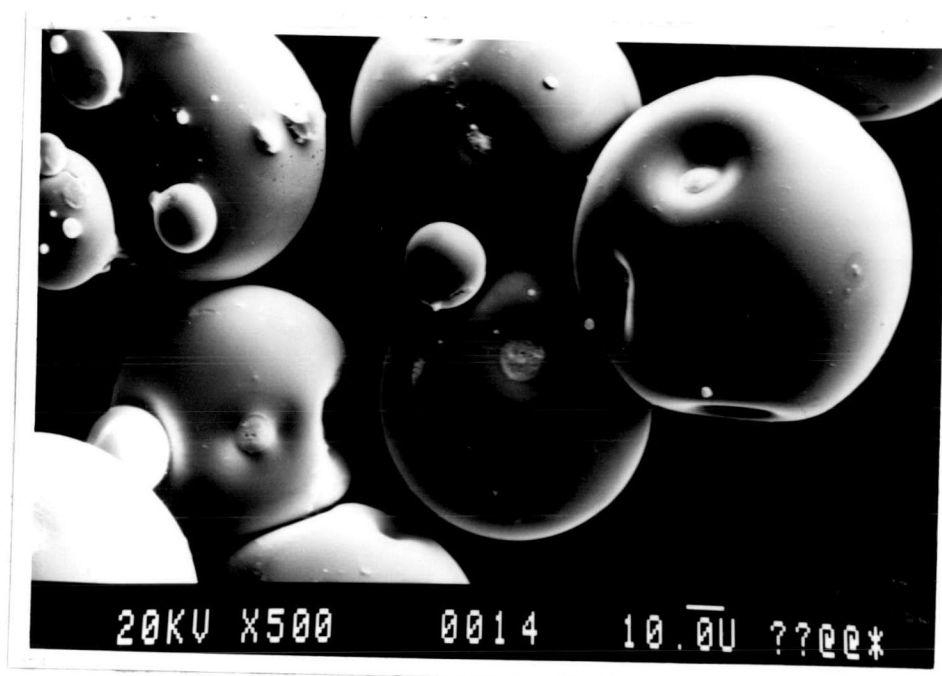
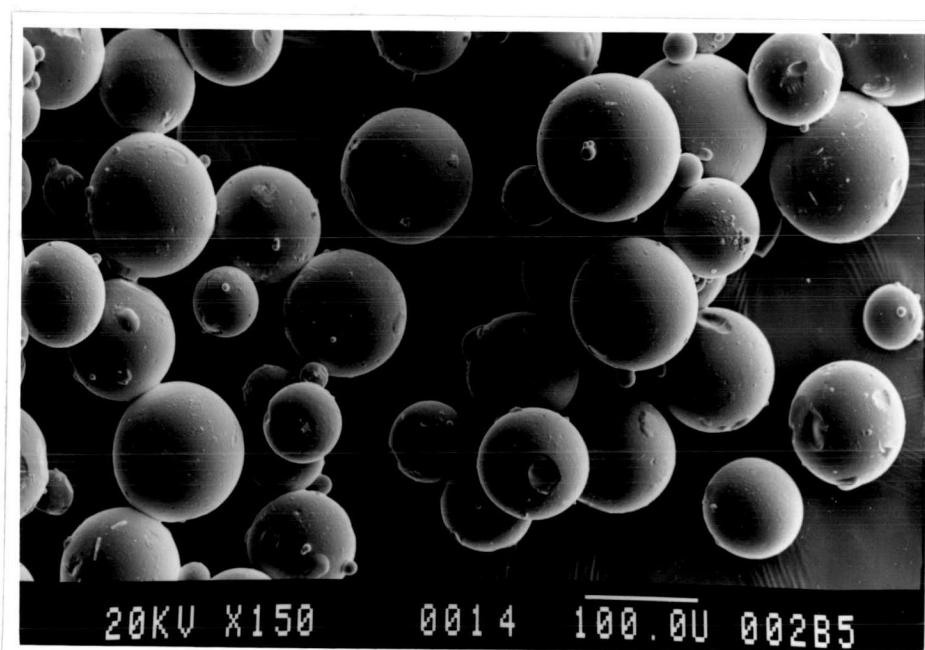Figure 4.24 SEM micrograph of the cross-linked copolymer, 0.025% N,N′-MBA

Figure 4.25 SEM micrograph of the cross-linked copolymer, 0.05% N,N′- MBA
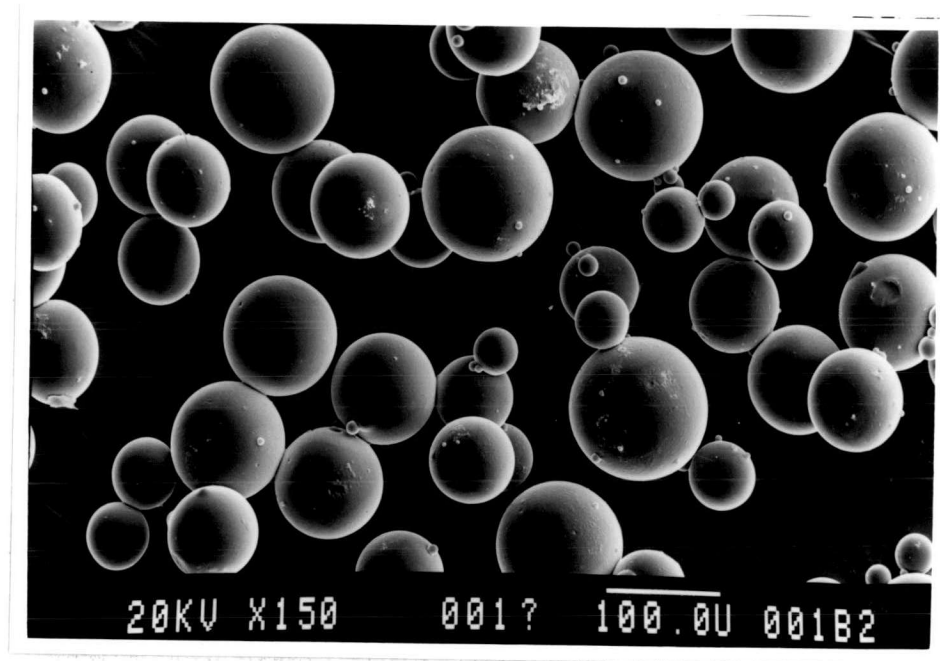
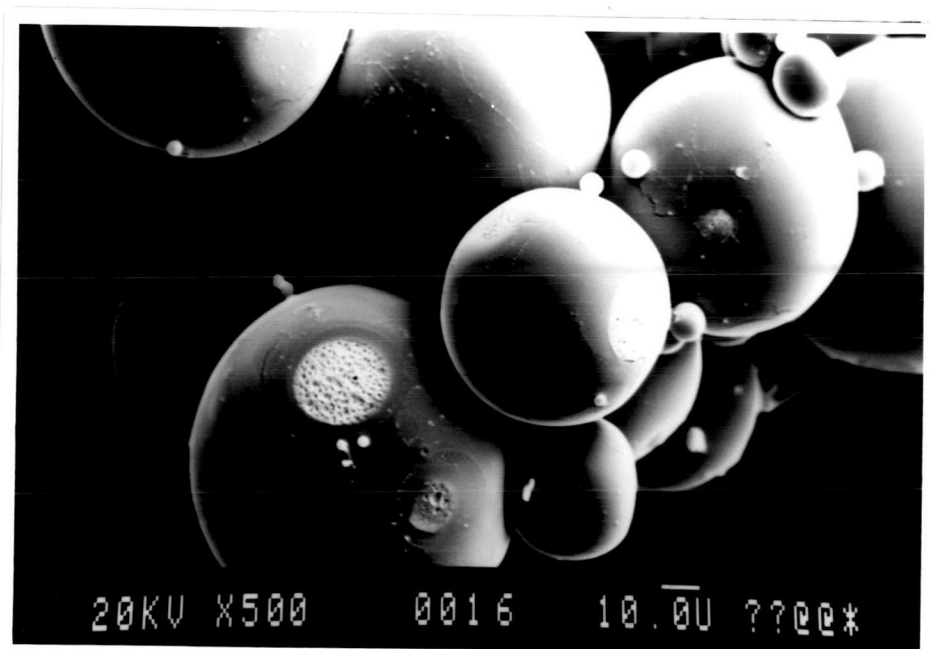Figure 4.26 SEM micrograph of the cross-linked copolymer, 0.075% N,N′- MBA

Figure 4.27 SEM micrograph showing the cellular structure of the copolymer beads at 500 x magnification.
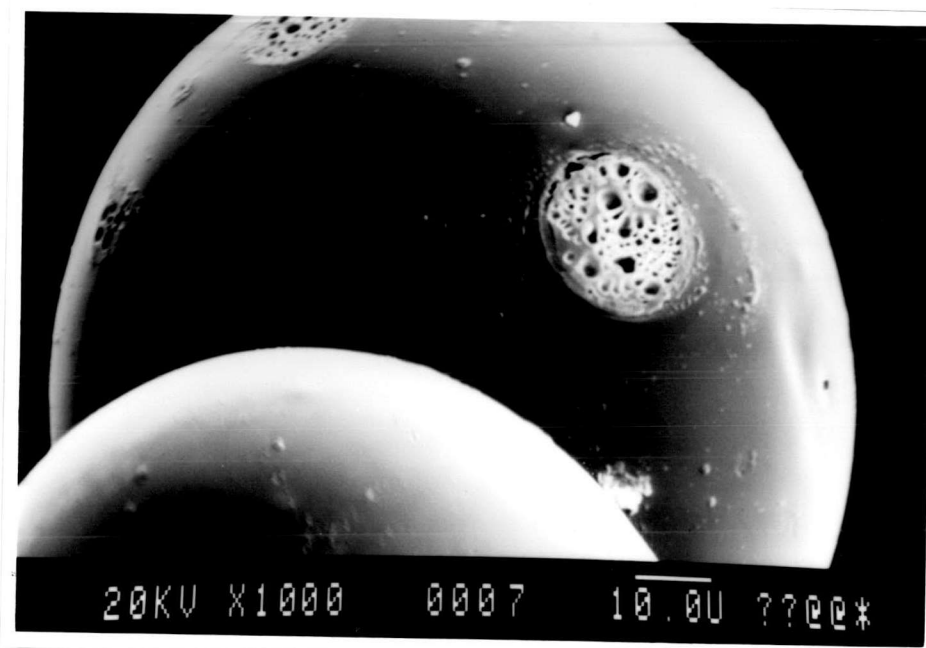
Figure 4.28 SEM micrograph showing the cellular structure of the copolymer
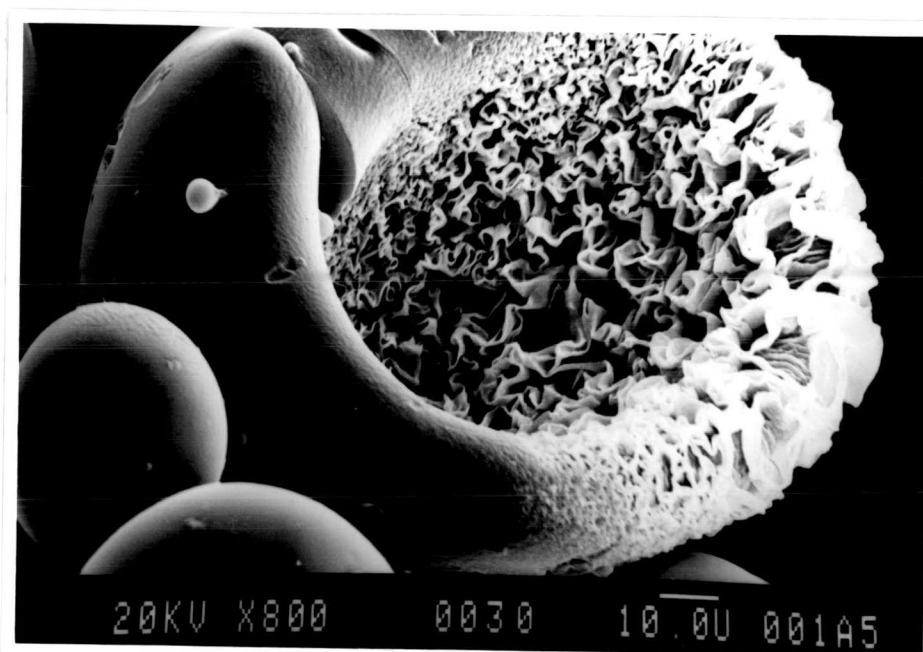beads at 1,000 x magnification.

Figure 4.29   SEM micrograph showing the huge cellular structure of the
copolymer beads at 800 x magnification.