CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The petroleum-based HWAPs are more attractive than modified starch-based superabsorbents due to their stability to microorganism and longer service life. Hence, recently many polymer scientists have paid attention to study and synthesize various kinds of HWAPs from petrochemicals. The major types of HWAPs which apparently progressed beyond the laboratory and usually disclosed in the patent literature are poly(acrylic acid) salts, polyether-based nonionic xerogellants, hydrolyzed polyacrylonitrile, poly(vinyl alcohol-sodium acrylate), and poly(isobutylene-*co*-disodium maleate) (28). The radical polymerizations used to synthesize the petroleum-based HWAPs, can be initiated by thermal- and redox-type initiators. In this research, the copolymer of acrylamide(Am) and potassium acrylate(KA) was synthesized by inverse suspension polymerization. The following were concluded:-

1. The concentration of Am:KA was varied from 10:90 - 90:10 molar ratio of the total monomer concentration of 7 molar using thermal initiator($(NH_4)_2S_2O_8$) of 1.4 g/l at 60 °C. The molar ratio of Am:KA at 71:29 provided a water-insoluble copolymer having the best water absorbency of 347 g/g whereas other ratios gave water-soluble copolymers.

2. The effect of polymerization temperature was investigated from 40-60 °C. It was found that at lower temperatures (40 and 45 °C) the polymerizations produced water-soluble products, but at higher

temperature (50 and 60 °C), they provided water-absorbing copolymers which can swell in aqueous solutions.

3. The concentrations of initiator($(NH_4)_2S_2O_8$) from 0.5-2.0 g/l of the suspension were studied at the polymerization temperature of 60 °C. It was found that polymerization initiated with the persulfateat 1.4 g/l provided the highest water-absorbing copolymer possessing the water absorbency of 347 g/g.

4. The concentrations of N,N´-MBA varied from 0.005-0.05 mole% based on the total monomer concentration were used to crosslink the copolymer by thermal initiation with $(NH_4)_2S_2O_8$ 1.4 g/l at 60 °C. The most appropriate concentration of N,N´-MBA was 0.04 mole% to produce the best crosslinked copolymer having water absorbency of 122 g/g. However, crosslinking with N,N´-MBA did not improve water absorbency of the copolymer comparing to the polymerization without crosslinking agent probably due to high crosslink density in the copolymer.

5. Crosslinked copolymers were also synthysized by inverse suspension polymerization with redox initiating system of $(NH_4)_2S_2O_8$: TMEDA (2:1 ratio by weight) at lower temperature (45 °C). The water absorbency of the crosslinked copolymers synthesized by redox initiation were compared to those by thermal initiation at the equal concentrations of N,N´-MBA. The appropriate concentrations of N,N´-MBA to crosslink the copolymer by redox initiation are 0.020 and 0.050 mole%.

6. All of the synthesized copolymers were measured for the water absorbency by swelling in distilled water. The best water-absorbing copolymer having water absorbency of 347 g/g in distilled water, was selected to test the effect of salt concentration

upon the water absorbency of the copolymer. The water absorbency of the copolymer decreases rapidly as the salt concentration increases due to the ionic strength of the solution which affects the equilibrium osmotic pressure of the system. In case of the divalent Mg^{2+} ions, the osmotic pressure equilibrium should reach earlier than in aqueous K^{+} solution, and Mg^{2+} ions may crosslink the gel by salt formation with the carboxylate groups on adjacent chains or chain segments of the copolymer and lower the water absorbency comparing to that in aqueous K^{+} solution.

7. The synthetic copolymers were characterized as follows:-

a. The functional groups of the copolymer were identified by IR. The spectrum reveals that the functional groups of the copolymer are similar to those of the hydrolysed polyacrylamide reported in the literature(38).

b. The structure of the copolymer was analysed by ^{13}C-Solid state NMR, ^{13}C-NMR and ^{1}H-NMR, but the exact structure cannot be elucidated.

c. The thermal properties of the copolymer were determined by DSC. The thermogram shows that the copolymer has two endothermic peaks. The T_{g2} at 193.52 °C corresponds to the T_g of poly(potassium acrylate) in the literature(30), but the T_{g1} at 74.77 °C is much lower than the T_g of polyacrylamide homopolymer, possibly caused by the emulsifier(Span 60) coated on the surface of the copolymer beads.

d. The surface morphology of the copolymer beads was studied by SEM. The SEM micrographs reveal that lumps are observed on the water-soluble copolymer beads whereas the crosslinked copolymer

beads are rather round in appearance. The cellular structure was also found in the crosslinked copolymer similar to that of a polyacrylamide gel(39).

5.2 Suggestion

5.2.1 The water-soluble copolymers obtained in Section 3.3.1 can be used as thickeners in printing pastes and flocculants in water treatment.

5.2.2 Synthesis of HWAPs by inverse suspension polymerization should be further studied as follows:-

a) other kinds of monomer should be used in the polymerization to synthesize the best HWAP e.g. acrylic acid, sodium acrylate, litium acrylate, ammonium acrylate, and etc.

b) the influence of the concentration of emulsifier(Span 60) upon the particle size of the copolymer bead should be investigated in the range of 0.5-2 wt% based on the dispersion medium.

c) other kinds of emulsifier having HLB values of about 2-12 which are conventionally used in inverse suspension polymerization, should be used in instead of Span 60 such as Span 20, Span 40, Span 80, Tween 80, and so on to find an appropriate kind of emulsifier to synthesize the HWAPs with good absorption rate.

d) study the influence of stirring intensity on the polymerization degree within the range of 600 - 1,500 rpm(13).

e) other kind of thermal initiators should be used in place of $(NH_4)_2S_2O_8$ because when an acrylic acid salt is polymerized with the water-soluble persulfate, crosslinking proceeds without using a crosslinking agent; instead when the water-soluble azo-type polymerization initiator is used, crosslinking may occur with difficulties or unlikely to take place(29). The examples of azo initiators are 2,2´-azobis-(N,N´-dimethylisobutyramidine) dihydrochloride, 2,2´-azobis-(2-amidino-propane) dihydrochloride, 2,2´-azobis-(N,N´-dimethyleneisobutyranil-ine), 4,4´-azobis(4-cyanopentane carboxylic acid) and 2-carbamylazo-isobutyronitrile.

f) study the pore characteristics by Mercury porosimeter, and determine the crosslink density of the copolymer bead.

g) determine the M_c value which is the influencial parameter of the water absorbency to make known the extent of crosslink.