Partially Hydrolyzed Polyacrylamide–Poly(N-vinylpyrrolidone) Copolymers as Superabsorbents Synthesized by Gamma Irradiation

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ABSTRACT: Partially hydrolyzed polyacrylamide-*co*-poly(*n*-vinyl pyrrolidone) used as a superabsorbent was prepared from acrylamide monomers exposed to γ-rays to become polyacrylamide that was subsequently partially hydrolyzed and was then copolymerized with *n*-vinylpyrrolidone to obtain a terpolymeric superabsorbent with a water retention value of 1100 times its dried weight. The total dose and dose rate along with the appropriate degree of hydrolysis were investigated for percentage conversion in each polymerization and the extent of water absorption. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 191–203, 1998

Key words: HPAM-POLY(NVP); Superabsorbent; EOR; Gamma Irradiation

INTRODUCTION

Oil is an important source of energy and a raw material in various manufacturing industries. Oil recoveries from the existing oil fields usually utilize superabsorbent polymers for an enhanced oil recovery (EOR) process. Partially hydrolyzed polyacrylamide (HPAM) has long been used in EOR processes. The degree of hydrolysis affects certain physical properties and thermal stability, especially in salt solutions of high ionic strength. Copolymers of HPAM polymerized with a comonomer of N-vinyl-2-pyrrolidone (NVP) can tolerate the hostile environmental conditions at exceptionally elevated temperatures. This article describes the preparation of these copolymers by γ-irradiation along with investigations of their properties.

EXPERIMENTAL

Materials

Acrylamide (AM, Baker) and NVP (Fluka) of AR grade were stored in a refrigerator before use. Methanol, commercial grade (BDH), was purified by fractional distillation at atmospheric pressure. Sodium hydroxide and acetone, both analytical grade (Merck), were used as received. General laboratory glassware and equipment were available for the experiment. The gamma source of Co^{60} (Gamma Cell 220) with 24,480 Curies was from Nordian International Canada.

Procedure

Polymerization of AM by γ-irradiation was carried out according to the technique in a previous article,[1] which also examined the effects of total

dose and AM concentration on percent conversion. Additional effects were investigated as follows:

Effect of Dose Rate and Total Dose on AM Polymerization

Various dose rates of 3.6×10^3, 5.34×10^3, and 11.9×10^3 Gy h^{-1} up to the total dose of 1.4 kGy were used to irradiate $2.5M$ AM solutions. The reaction products of polyacrylamide (PAM) were hydrolyzed by placing 5 g PAM in a 20% NaOH solution at 70°C for 4 h to obtain the properly hydrolyzed PAM for the subsequent copolymerization with NVP. The monomer conversion and the degree of hydrolysis were measured. Likewise, polymerizations at a fixed dose rate of 11.9×10^3 Gy h^{-1} to give the total doses of 0.1–2.0 kGy in increments of 0.1 kGy were also performed.

Determination of the Hydrolysis Degree of PAM

The hydrolysis degree of PAM to HPAM, determined by the semimicro Kjeldahl method, gives the nitrogen content in the polymers. The difference in the nitrogen content before and after the hydrolysis reaction (PAM and HPAM) was calculated as the degree of hydrolysis.

Effect of Total Dose and Dose Rate on Copolymerization of HPAM with NVP by γ-Irradiation

Five grams of HPAM mixed with 100 cm^3 deionized distilled water was placed in a 500 cm^3 reactor. The system was stirred at 400 rpm at 30°C for 30 min in a N$_2$ atmosphere. Then, the system was subjected to γ-irradiation. The copolymerizations of HPAM with NVP by γ-irradiation with a fixed total dose of 10 kGy at three dose rates (3.6×10^3, 5.3×10^3, and 11.9×10^3 Gy h^{-1}) were carried out. Another set of copolymerizations was performed at a fixed dose rate of 11.9×10^3 Gy h^{-1} to various total doses of 8, 9, 10, 11, or 12 kGy. HPAM and NVP concentration effects on the degree of hydrolysis were performed based on the previous work of Kiatkamjornwong and Suwanmala.[1] The percent conversion of the copolymerization and water absorption were investigated.

Characterization of the Polymers

Determination of Percent Conversion

The polymer and copolymer were weighed. The change in the weight of the monomer respective to the polymer was calculated to yield the percent conversion.

Water Absorption in Distilled, Deionized Water

Water absorption of the unhydrolyzed PAM, hydrolyzed PAM, and copolymers synthesized from various HPAMs were determined according to the technique described in a previous article.[2] The effects of oven drying and freeze drying on the extent of water absorption were studied.

Effect of Saline Solution on Water Absorption

NaCl and MgCl$_2$ were used as the model salts for observing salt effects on the water absorption of the modified AM–pyrrolidone copolymer. The NaCl concentrations of $1.7 \times 10^{-2}M$ (0.1% w/v), $8.56 \times 10^{-2}M$ (0.5% w/v), $1.7 \times 10^{-1}M$ (1.0% w/v), and $3.42 \times 10^{-1}M$ (2.0% w/v) were used for the monovalent salt effect. For the MgCl$_2$ solution, $1.05 \times 10^{-2}M$ (0.1% w/v), $5.25 \times 10^{-1}M$ (0.5% w/v), $1.05 \times 10^{-1}M$ (1.0% w/v), and $2.1 \times 10^{-1}M$ (2.0% w/v) were used to determine the divalent salt effect on water absorption.

Wicking Time of the Copolymer

A funnel composed of a 100-mesh aluminum screen was connected to a graduate burette through a rubber tube. The levels of the aluminum screen and of the burette were adjusted to the same zero position. Distilled deionized water was filled into the burette until the water level reached the zero level. The aluminum screen was then thoroughly wetted. Dried copolymer (0.1 g) was dropped onto the wet aluminum screen and it, consequently, swelled. The time required for 0.1 g of the copolymer to be fully wetted was regarded as the wicking time, which was then recorded.

Thermal Properties of PAM, HPAM, and HPAM–NVP at Various Degrees of Hydrolysis

Thermogravimetric analysis was used to study the thermal properties of the superabsorbent. The temperature range of 50–650°C under a nitrogen atmosphere with a heating rate of 20°C min^{-1} was programmed to record changes in temperature of the PAM, HPAM, and HPAM–NVP at various degrees of hydrolyses.

RESULTS AND DISCUSSION

AM and its polymers are usually water-soluble. Polymerization of AM carried out in a homogeneous medium containing water can be considered
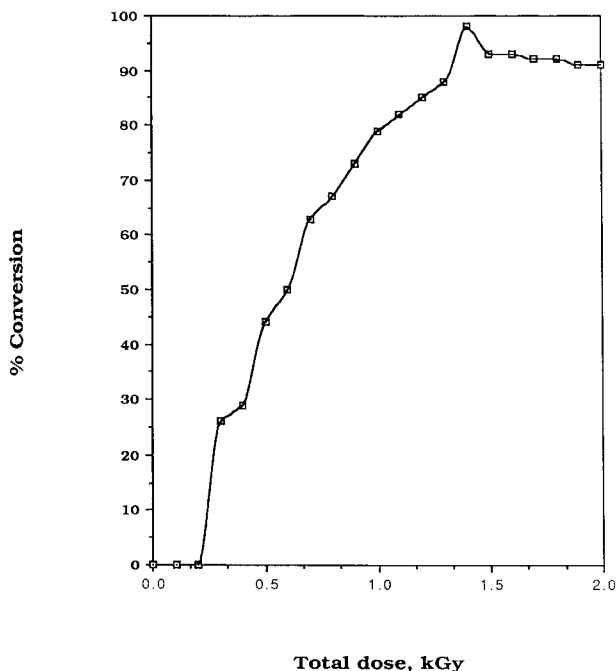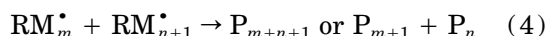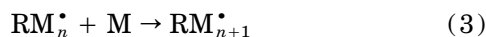
Figure 1   Effect of total dose on percent conversion.

by the radiolysis of water, which produces radicals interacting with the AM monomers under the following reactions:

$$H_2O \xrightarrow{\gamma\text{-rays}} R^{\bullet} \quad (1)$$

$$R^{\bullet} + M \rightarrow RM^{\bullet} \quad (2)$$

$$RM_n^{\bullet} + M \rightarrow RM_{n+1}^{\bullet} \quad (3)$$

$$RM_m^{\bullet} + RM_{n+1}^{\bullet} \rightarrow P_{m+n+1} \text{ or } P_{m+1} + P_n \quad (4)$$

The extent of polymerization is then controlled by the production of radicals (dose rate) from water under the effect of total irradiation (total dose, a combined product of dose rate and irradiation time). The polymers obtained in each step were characterized by FTIR to identify the existing functional groups. The results indicate the existence of PAM, HPAM, and the random copolymers of HPAM and NVP.[3]

Effects of Total Dose and Dose Rate on PAM Polymerization

Previous results of Kiatkamjornwong and Suwanmala[1] reporting the effect of the total dose at a fixed dose rate of 1.19×10^4 Gy h^{-1} to polymerize AM to PAM are shown in Figure 1, from which the optimum total dose of 1.4 kGy gave the highest percent conversion. The effect of the dose rate on

AM polymerization carried out at a fixed total dose of 1.4 kGy is illustrated in Figure 2.

The total doses of 0.1 and 0.2 kGy could not produce any PAM, that is, the doses were too low to initiate any reaction. This behavior at low doses, where the radicals formed were only to a small degree involved in the formation of the polymer and the growth of chains, may indicate that the polymerization was completely inhibited by the reaction with a possible low content of oxygen contamination in the system, which decreased with increased total dose. When the oxygen or other radical scavenger was consumed, then the polymerization could occur. The higher total doses overcome the induction effect and promote the increase in percent conversion of the monomer. This observation is analogous to the work of many other researchers elsewhere. The second portion of the reaction beginning with total doses of 0.4– 1.4 kGy gave a linearly increasing rate. The highest conversion is obtained at the total dose of 1.4 kGy. Total doses higher than 1.4 kGy would give the plateau of the conversion where increases in total dose would produce a constant conversion or even a slight decrease in conversion. At a higher total dose and high percent conversion, termination is a diffusion-controlled reaction. The k_p value in r_p [eq. (6)] becomes sufficiently affected so that $r_p/[M]^{3/2} \cdot [D^{\bullet}]^{1/2}$ begins to level off or decrease. The decrease in rate, sometimes referred to as
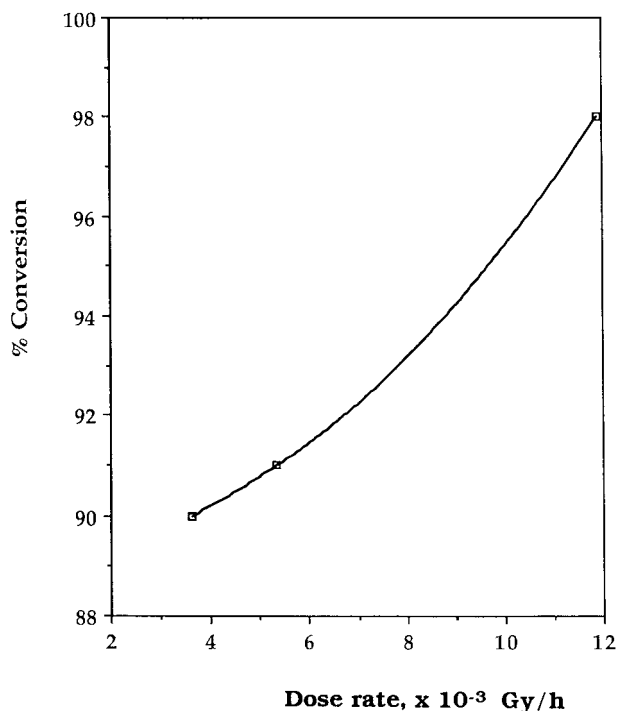

Figure 2   Effect of dose rate on percent conversion.

the glass or vitrification effect, can be extremely pronounced depending on the reaction temperature.[4] The glass transition temperature of a polymerization reaction mixture increases with conversion of monomers to polymers. Polymerization can stop appreciably short of complete conversion when polymers have a glass transition temperature exceeding the reaction temperature. The basic sequence of polymerization still comprises initiation, propagation, and termination. With increasing conversion, the rate of initiation could be written as follows:

$$r_i = D^\bullet(G_m(R^\bullet)[M] + G_p(R^\bullet)[P]) \quad (5)$$

where r_i is the rate of initiation; $D^\bullet$, the dose-related rate of generating radicals; $G_m(R^\bullet)$, the radical yield of the monomer; $[M]$, the concentration of the monomer; $G_p(R^\bullet)$, the radical-chemical yield of polymerization, i.e., molecules transformed into polymers per 100 eV of absorbed energy; and $[P]$, the concentration of the polymer. The equation indicates that the higher the dose rate, the greater the rate of initiation, and, thus, a higher rate of conversion is possibly obtained. The rate of polymerization as shown in eq. (6) depends on the square root of $G_m(R^\bullet)$ and the dose rate, but on $[M]^{3/2}$,[5] a concentrated monomer was required for the higher rate of the polymerization (conversion):

$$r_p = k_p[G_m(R^\bullet)D^\bullet/100N_A]^{1/2}[M]^{3/2}/k_t^{1/2} \quad (6)$$

where r_p is the rate of polymerization; k_p, the rate constant of propagation; k_t, the rate constant of termination; and N_A, Avogadro's number. This can be observed from the result that the higher concentrations of AM gradually increase the conversion. From the main features of the free-radical mechanism in radiation-induced polymerization, one generally finds the following conclusion: The polymerization rate is proportional to the dose rate to the power 0.5; the molecular weight of the polymer is proportional to the dose rate to the power 0.5; and the polymerization is inhibited by typical free-radical inhibitors such as oxygen.

A viscosity increase was observed during the conversion with increasing absorbed energy until gelation was attained during 50–70% conversion. It was shown that $r_p \alpha D^{\bullet 1/2}$ and this relation holds even in the stage of the gel effect. The bimolecular termination of macroradicals predominates. Basically, an increase in total dose enhances the formation of radicals in the reaction mixture, that is, monomers, acetone, hydrogen, and hydroxy radicals. The hydrogen and hydroxy radicals could perform the chain-transfer reaction to reduce the percent conversion, especially at the higher total doses. The formation of the hydrogen and hydroxy radicals of water, caused by dissociation, electron capture, electron ejection, and excitation reactions, are enhanced at higher total doses[6] due to that their relatively higher G values ($G(H^\bullet) = 0.55$, $G(OH^\bullet) = 2.8$, and $G(e_{aq}^-) = 2.7$). A homografting reaction, the reaction of grafting onto its own polymer, would probably occur at high degrees of conversion. The endlinks theory would still have the same effect for the formation of trifunctional joining points for the process of network forming. Under such conditions, the recombination of the two increasing, grafted side chains forms the network.

Because of the limitation of the irradiator configuration, the dose rate could be easily adjusted for further experiments, because the irradiator came with a fixed distance between the source and the sample site. A lead block was used to reduce the intensity of the dose, which can only give smaller dose rates: The smaller dose rates that we used were 5.34×10^3 and 3.6×10^3 Gy h^{-1}. The extent of total dose absorbed by the reaction mixture depends, to a greater extent, on the dose rate, that is, the rate of generating radicals for the polymerization controls the efficiency of the initiating stage to give the monomer radicals that are subsequently propagated and finally terminated to give the PAM polymer. The total dose that the monomer can absorb would certainly account for the irradiation time needed to the desired dose. Generally, an increase in dose rate enhances the formation and density of the primary events involved in the irradiation. For the effect of the dose rate, shown in Figure 2, an increasing percent conversion was found with a higher dose rate. This implies that the yield of the stable reaction products increased insignificantly, that is, the molecular primary products are marginally increased.

PAM could be very useful as a superabsorbent polymer when it is properly hydrolyzed. Apart from IR spectroscopy, ^{13}C-NMR and elemental analysis can be used quantitatively to measure the degree of hydrolysis of the polymers without the need to accurately measurement the weight of the sample. The semimicro-Kjeldahl method employed is an easier technique to determine the nitrogen content resulting from the hydrolysis.

Temperature is an important controlling factor to drive the hydrolysis to take place. For higher reaction temperatures, more changes in the am-

ide groups on the PAM backbone to form the carboxylate groups of partially hydrolyzed PAM are observed, as already shown in eq. (7). For prolonged heating periods, the degree of hydrolysis of PAM increases with the reaction time. It is common that the reaction can proceed further with prolonged time to reach the desired hydrolysis, that is, more PAMs could be hydrolyzed to form carboxylate groups.

A higher degree of hydrolysis could also be achieved by increasing the concentration of sodium hydroxide that changed the amide groups to become the carboxylate groups. The proper ratio between the amide (x) and the carboxylate $(n - x)$ groups, in eq. (7), is the key property for the superabsorbent polymer, depending on the level of water absorption required. Anionic PAM with 20–30% ionized groups is the most common of the high molecular weight polymers used in mining and other industries.[7] This property is governed by several parameters, including the reaction time and alkaline concentration. The effect of the quantity of PAM on the degree of hydrolysis at the specific reaction conditions of 3 h, 70°C, and 20% NaOH (w/v) is presented, which shows that the PAM concentrations higher than 5 g would not appreciably increase the degree of hydrolysis under the present conditions[1]:
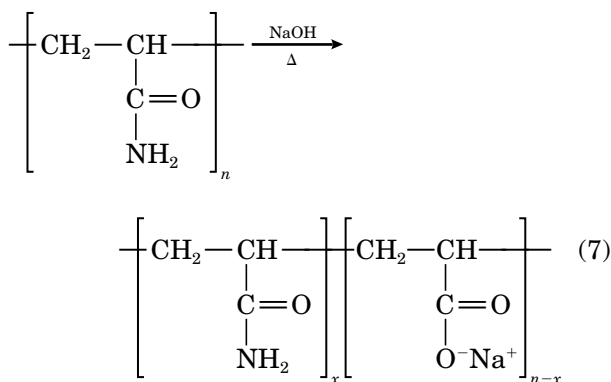
Copolymerization of Partially Hydrolyzed PAM and 1-Vinyl-2-pyrrolidone

Effect of Dose Rate and Total Dose on Copolymerization Conversion and Water Absorption

Figures 3 and 4 show the results of dose rate and total dose, respectively, on conversion and water absorption of the copolymer of HPAM–NVP. Water absorption of the unhydrolyzed PAM and the hydrolyzed one were only 18 and 24 g g^{-1}, respec-
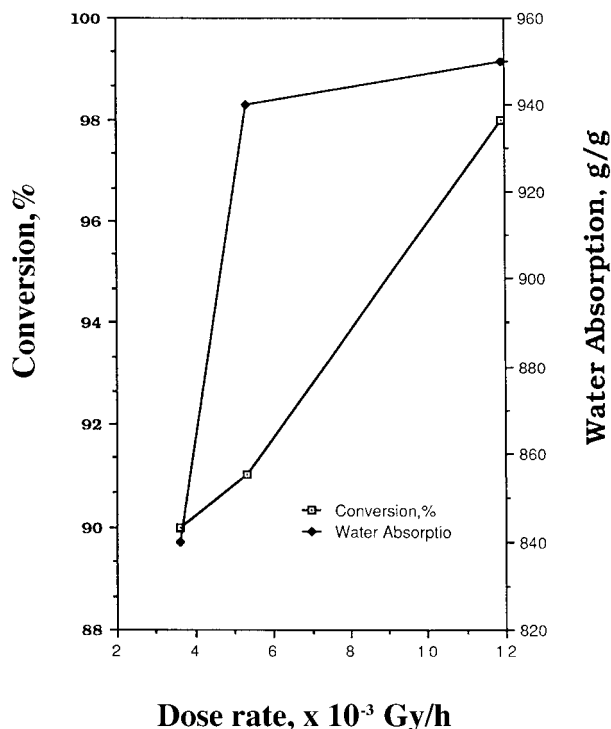

Figure 3 Effect of dose rate on copolymerization and water absorption of HPAM–NVP.

tively. This implies that further modification of the HPAM is essential for higher water absorption.

AM polymers are the crosslinking polymers under irradiation. They contain a backbone of $—(CH_2—CH—R)_n$ which has a less steric hindrance effect, as the side groups are quite free to arrange themselves spatially along the chain. When the rupture of hydrogen or a substituent occurs in the chain by the action of radiation, the resultant polymer radicals may react with polymer radicals at adjacent sites on neighboring chains and thus the crosslinking of the two polymer chains is formed.[8] In addition, an NVP monomer has better chances to copolymerize with those active sites. The resulting copolymer is water-insoluble but only swells, which is a nature of the crosslinking polymer.

At a fixed total dose of 10 kGy, increasing the dose rate from 3.0×10^3 to 11.9×10^3 Gy h^{-1}, the conversion increases from 69 to 79% and the water absorption increases from 890 to 950 g g. At higher dose rates, more radicals were generated to produce polymer growing chains, $G_p(R^\bullet)$. Radical reactivity between the HPAM and the NVP is naturally unequal, as the propagating HPAM chains are polymer radicals whose molecular dimension is much bigger than that of NVP,
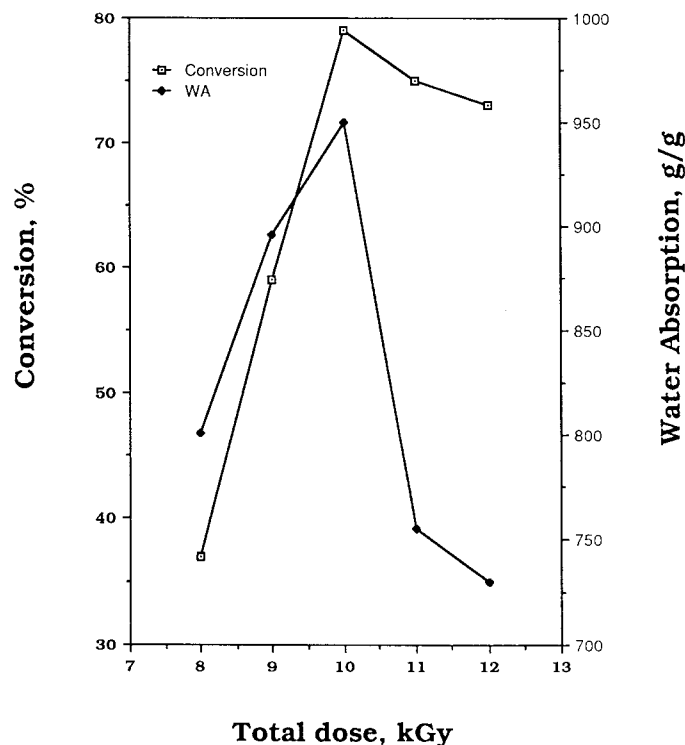
Figure 4 Effect of total dose on copolymerization and water absorption of HPAM–NVP.

a monomer. Active sites at the HPAM backbone were initiated by γ-rays and were sites onto which the NVP radicals could diffuse and collide to form random copolymers. The reactivity of a monomer toward a polymer radical depends most importantly on the polymer radicals and the incoming monomer. The gel effect due to the presence of HPAM in the bulk system further decreases the mobility of the HPAM molecules, resulting in a decrease in reactivity of the HPAM and an increase in reactivity of the NVP. Then, copolymerization of HPAM–NVP can occur with more NVP units added to the polymer chain.

The effects of the total dose and dose rate on conversion and water absorption in distilled deionized water are shown in Figures 2 and 3. It must be mentioned that the uncrosslinked PAM and its hydrolyzed polymer can normally dissolve in cold water while the copolymer of HPAM and NVP cannot dissolve in water. This finding may indicate the existence of certain crosslinking sites on the polymer backbones due to radiation-induced crosslinking. The present copolymerization can be thus be regarded as a random copolymerization as the HPAM is a high molecular weight polymer that is randomly copolymerized by the 1-vinyl-2-pyrrolidone. The lack of crystallinity to

the desirable degree points to the heterotactic nature of the polymers studied, another indication of the random copolymerization.[9] The amount of conversion of the monomer varied from 37 to 79%, depending on the dose. The highest conversion occurred at the total irradiation dose of 10 kGy; beyond that, the conversion decreased, which might be a chain-scission effect of the polymer. Total doses lower than that also gave lower conversions and much lower values of water absorption. The radical yields from the radiolysis of the HPAM (G value) must be as much as possible in excess of that of the monomer (NVP). It seems that this condition is fulfilled. The higher irradiation dose gave a large amount of radiolysis products (in the absence of oxygen): H$^\bullet$ with a $G(\text{H}^\bullet)$ of 0.55, OH$^\bullet$ having a $G(\text{OH}^\bullet)$ of 2.8, and $G(e_{\text{aq}}^-)$ of 2.7 at pH 4–7 that could initiate homopolymerization rather than random copolymerization.[10] The H$^\bullet$ and OH$^\bullet$ are the species frequently chain-transferred to growing chains, which, consequently, terminate the copolymerization reaction. Therefore, at higher doses, a greater amount of poly(1-vinyl-2-pyrrolidone) (PVP) is possibly formed at the expense of the copolymerization. At the lower doses, few radicals were generated that could only produce a small number of PVP growing chains to be copolymerized with the active sites of the
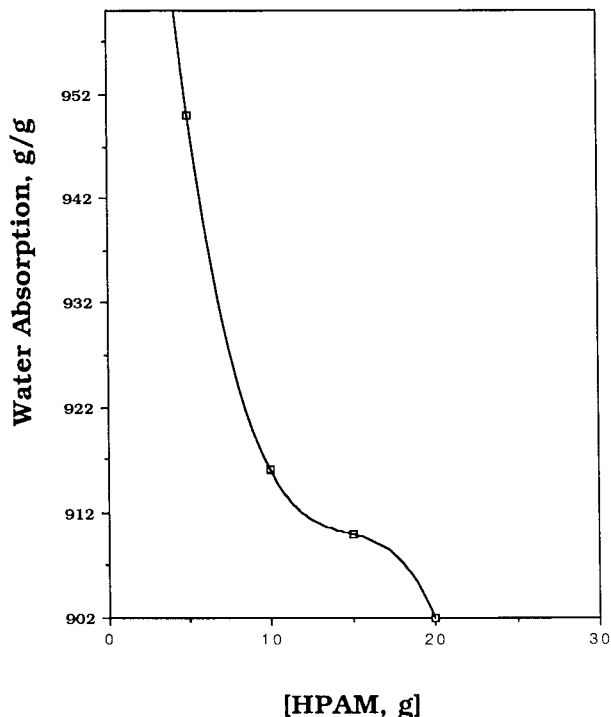
Figure 5   Effect of concentration of HPAM with NVP on water absorption.

HPAM because they are not sufficiently activated. The effect of the concentration of HPAM on random copolymerization is shown in Figure 5.

Effect of Concentration of HPAM and NVP for Copolymerization on Water Absorption

The concentrations of HPAM and NVP play an important role in copolymerization. Figures 5 and 6 show the effect of each reactant's concentration on water absorption. Since HPAM is insoluble due to crosslinking, we cannot state its concentration in molarity. One can see that HPAMs (20, 15, 10 g) copolymerizing with a constant weight of NVP give a relatively constant value of water absorption. The amount of HPAM influences the copolymerization in that a content higher than 5 g would not affect the extent of random copolymerization or the extent of water absorption.

The water absorption of the copolymer was found to be directly related to the percent conversion. The extent of water absorption strongly depends on the degree of network crosslinking and elasticity. Such properties are governed by the amount of NVP to be randomly copolymerized and crosslinked between two HPAM chains. The effect of the quantity of 1-vinyl-2-pyrrolidone on water absorption for a total dose of 10 kGy and 11.9 $\times$ 10^3 Gy h^{-1} dose rate is also shown in Figures

5 and 6. For 5 g of HPAM copolymerizing with 0.47, 0.94, 1.41, and 1.88M of NVP, the NVP concentration shows a stronger affect on water absorption especially at the NVP concentration of 0.94M. It is anticipated that the lower concentration of NVP could not produce a stronger gel (crosslinking caused by an autoacceleration reaction) while the concentrations higher than 1.41M produce a rigid chain that would not facilitate a higher amount of water absorption. One can see that the NVP limit was found at 1.41M. The NVP can limit the level of PAM hydrolysis when used under severe conditions, such as high temperature and high ionic strength of a salt solution.

Effect of Degree of Hydrolysis and the Type of Drying Method on Water Absorption Behavior of the Copolymers: Dependence of the Extent of Water Absorption on the Degree of Hydrolysis

Since both HPAM and the copolymer of HPAM–NVP are water-absorbing polymers, it is very important to determine the extent of water absorption as a function of the degree of hydrolysis of the final products. The water absorption of the HPAM (about 24 g g^{-1}) is independent of the degree of hydrolysis and not so much higher than that of its precursor, the unhydrolyzed form (18 g g^{-1}). Therefore, HPAM is not really a useful water-absorbing polymer for the present pur-
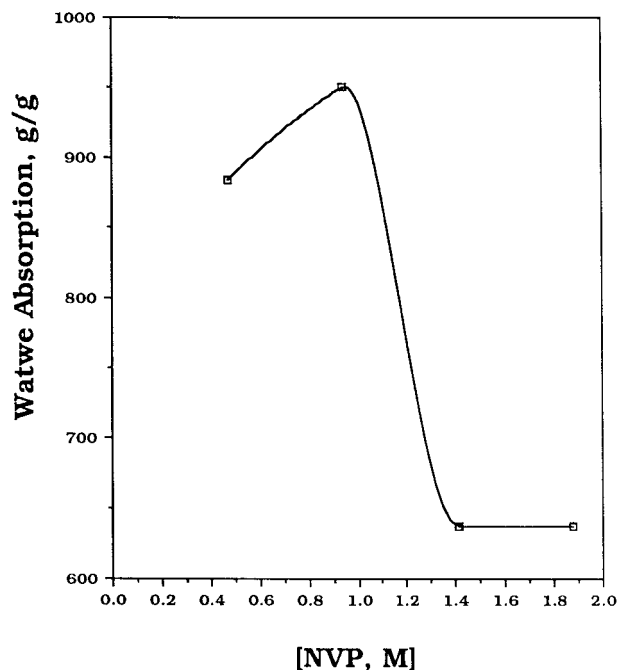

Figure 6   Effect of concentration of NVP with HPAM on water absorption.

poses. Nonetheless, Khune et al.[11] suggested two possible approaches for improving HPAM-type polymers by stiffening the polymer backbones and substituting alkyl groups for one or both of the hydrogens on the amide nitrogen. Neither the AM nor the NVP homopolymer could be useful on its own as an EOR material.[12] Nonetheless, they can be used as flocculating agents or in other applications other than as superabsorbent polymers. Unlike HPAM and PVP, the random copolymers of HPAM and NVP seem to be useful superabsorbent polymers due to their high water absorption values and high viscosity. The viscosity of the random copolymers measured by the same technique as above was 2,140, 2,050, 2,042, 2,010, 2,004, 1,940, and 1,916 mPa s for the 64, 71, 72, 76, 77, 80, and 84% hydrolyzed HPAM, respectively. An autoacceleration reaction during the course of polymerization can occur, that is, the gel formation during the reaction can be found at 50–80% conversion. This effect is possibly explained by a decrease in the termination rate constant for polymer accumulation.

At low degrees of hydrolysis, the number of the carboxyl groups is very low and randomly distributed[13] in that any hydrogen bonds formed would not be able to sustain a stable intramolecular complex. At low degrees of hydrolysis, the expansion of the HPAM coils is less than at the higher degrees. Therefore, it is not the dissociation of the —COONa groups that prevents interactions with PVP. This could possibly suggest that there is a critical number of —COONa groups required for complexation with PVP. The interactions between —COONa groups of the HPAM and the bulky functional groups of the PVP could cause steric hindrance, resulting in decreased mobility of the complex and a more rigid chain. The hydrogen bonding of PVP with the —COONa of HPAM will be strong on account of the high electronegativity of the oxygen of PVP due to the presence of the nitrogen atom.

Such interactions are absent only when all the —COONa group of the HPAM are ionized. Interpolymer interactions between PVP and —COONa groups, which are favored over the intrapolymer interactions between the amide and the acid groups, are a vital contribution to high water absorption. When the degree of hydrolysis is high, there is no such interaction between PAM and PVP. A possible explanation of this phenomenon lies in the number of the amide and carboxylate groups present on the polymers as stated. At low degrees of hydrolysis, the number of the amide groups is much higher than that of the carboxyl-

ate groups. Interactions between the few widely scattered —COONa groups and the 1-vinyl-2-pyrrolidone groups will certainly be weak. PVP will interact slightly with the amide groups, and this weak interaction results in a marginal decrease in the segmental mobility of the HPAM. As the number of —COONa groups increases with higher hydrolysis (the HPAM containing a low content of amide groups), interaction between the —COONa and PVP will increase. Under these conditions, the number of amide groups is apparently too low for any significant interaction with PVP and interactions between PVP and the —COONa groups dominate. The higher the degree of hydrolysis, the larger the number of hydrogen bonds and, therefore, the lower the segmental mobility of the complex.

Effect of Degree of Hydrolysis and Drying Methods on Water Absorption and Wicking Time

The effects of the degree of hydrolysis, drying method, oven drying at 65°C or freeze-drying, and wicking times are shown in Figures 7 and 8. In these figures, the water absorption and wicking times of the absorbent polymers are shown. The oven-drying method gives a product with less water absorption than the freeze-drying method because of the induced crosslinking reaction during drying.[14] The wicking times of the freeze-dried copolymers were longer. This can be attributed to the specific surface of the copolymer for the absorption, which is one of the parameters controlling the wicking time.

Effect of Saline Solutions on Water Absorption

Figure 9 shows the water-absorption capability of the modified poly(acrylamide-co-pyrrolidone) in the NaCl and MgCl$_2$ solution. The water-absorption efficiency of the copolymer is very dependent on the salt concentration and the oxidation state of the metal ion, that is, the water absorption decreases in the salt solution and it decreases much more rapidly in the MgCl$_2$ solution than in the NaCl solution. The higher the concentration of the salt, the greater the ion concentration. Theoretically, the ions attached to the macromolecule network in the copolymer (gel) are immobile and are considered to be separated from the external solution by a semipermeable membrane, which confines the immobile ions, but gives passage to water and all simple ions. The excess concentration of mobile ions in the gel phase can be calculated using Donnan's equilibrium model. This excess concentration is directly proportional to the osmotic pressure differential and is assumed to be
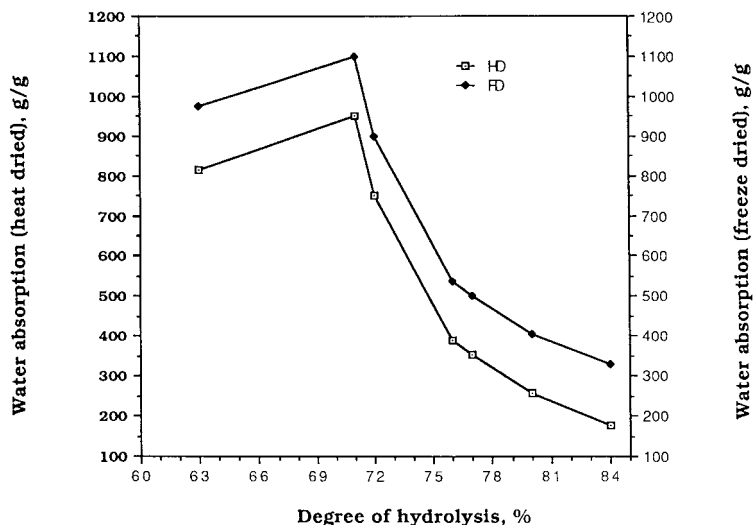
Figure 7 Effect of degree of hydrolysis and drying method on water absorption.

directly proportional to degree of swelling, that is, to the water absorption.[15]

The copolymer can be considered as a strong electrolyte that contains the sodium salt of poly-(acrylic acid) as polyacrylate and polycarboxamide (PAM). The gel ionization has a significant effect on the water-absorption capacity. When the copolymer is in a NaCl solution, the surface of this material behaves as a semipermeable membrane. To maintain electrical neutrality on both sizes of the membrane, Na^+ and Cl^- ions have to diffuse through the membrane from the external solution to the interior of the gel. The amounts of Na^+ and Cl^- diffusing from the external solution to the interior of the gel is inversely proportional to the concentration of nondiffusible ions. The unequal distribution of the diffusible ions (Na^+ and Cl^- ions) in the two compartments is the Donnan effect,[15] assuming that the copolymer has the same behavior as that of the sodium salt of protein.

The osmotic pressure of the system is now determined by the difference between the number of particles in the external solution and that in the interior of the gel. We assume that Na^+ ions in the interior of the gel have the same concentration (mol ion L^{-1}) as that of polycarboxylate. The osmotic pressure of the system can be described as follows:

$$\Pi = (2a^2 + 2ab)RT/(a + 2b) \qquad (8)$$

where Π is the osmotic pressure (atm); a, the concentration of polycarboxylate and Na^+ ions in
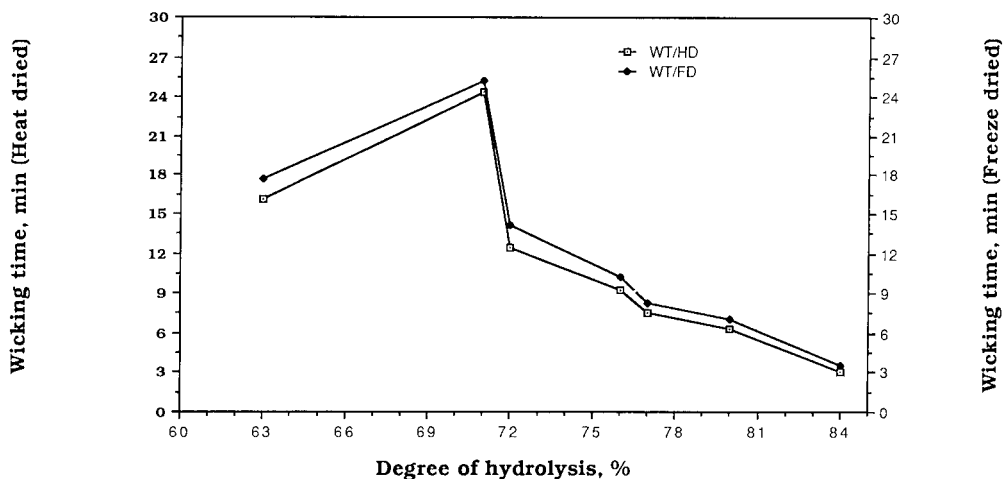

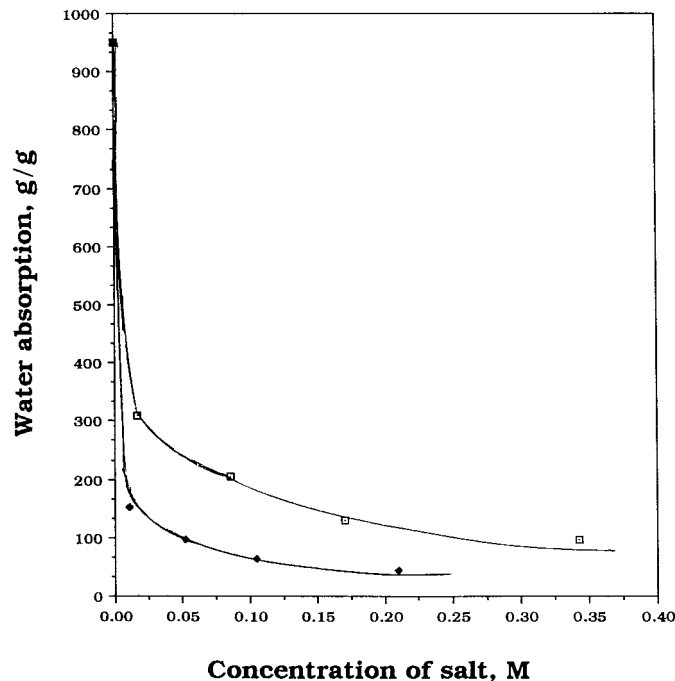**Figure 8** Effect of degree of hydrolysis and wicking time on water absorption.

Figure 9   Effect of saline solutions on water absorption: ($\square$) NaCl and ($\blacklozenge$) MgCl$_2$ solutions.

the interior of the gel (mol ion L^{-1}); b, the concentration of Na$^+$ and Cl$^-$ ions in the external solution (mol ion L^{-1}); R, the gas constant (8.314 JK^{-1} mol^{-1}); and T, the temperature (degrees Kelvin). The water intake by the semipermeable membrane reduces the osmotic pressure until equilibrium between the ions is achieved.

According to eq. (8), when the concentration of the salt solution increases, the osmotic pressure then decreases. With more ions, there is less water absorption. A MgCl$_2$ solution provides Mg^{2+}, which is a divalent ion, so the osmotic pressure of the system is much lower than for a NaCl solution. Additionally, the osmotic pressure differential between the interior and external solutions reaches equilibrium much faster than for NaCl solutions.

In an oil-producing well environment, a similar effect is expected as it contains many types of ions. The use of HPAM–NVP copolymers in the well also results in a reduction in water absorption. HPAM is a type of electrolyte that can interact quite strongly with ions in a solution. Since the PAM chain is flexible, it can respond to the ionic strength of the salt solution better than can HPAM. Because the water absorptions of unhydrolyzed PAM and HPAM were 18 and 24 g g, respectively, the incorporation of PVP onto the HPAM chains assists the water absorption as shown in previous sections. It is therefore essential to have this type of highly water-absorbing
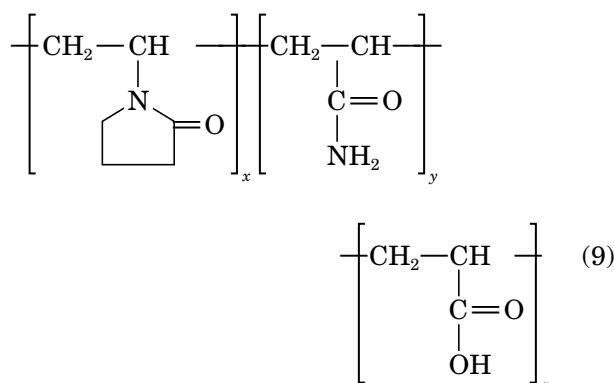
superabsorbent as a terpolymer for use in an environment containing a wide variety of concentrated salt solutions with high ionic strength.

Thermal Behavior of the Copolymer of HPAM and NVP

The degree of hydrolysis (charge-to-mass ratio) is considered to be important for several physical properties such as adsorption, shear stability (viscosity loss), and thermal stability. The work of Moradi-Araghi and Doe[16] reported that the hydrolysis of the amide group of HPAM would continue at elevated temperatures (121°C). As a consequence, the present work investigated the higher degrees of hydrolysis to avoid the posthydrolysis reaction. We are confident that the superabsorbent obtained by HPAM copolymerized with NVP should be stable at the elevated temperatures when they are used in the EOR process.

Stahl et al.,[13] studied thoroughly and systematically the approach to the formulation of a new synthetic polymer for oil recovery used at high temperatures and salinity (121°C) in synthetic sea water at 33,756 ppm of the total dissolved solids. They found that PAM, a number of PAM copolymers, and other synthetic copolymers of poly(vinyl ether), polyvinylpyrrolidone, and poly-(ethylene oxide) precipitated or showed serious viscosity loss at 121°C. However, they did find

that copolymers of 1-vinyl-2-pyrrolidone and AM do not precipitate at this temperature. The notational primary structure of the copolymer, poly-(vinylpyrrolidone-*co*-acrylamide), is thus illustrated in eq. (9) as follows:

$$\left[CH_2-CH \atop \underset{x}{\underset{|}{N}=O} \right] \left[CH_2-CH- \atop \underset{y}{\underset{|}{\underset{NH_2}{\overset{|}{C}=O}}} \right]$$

$$\left[CH_2-CH \atop \underset{z}{\underset{|}{\underset{OH}{\overset{|}{C}=O}}} \right] \quad (9)$$

The notational structure of the poly(vinylpyrrolidone-*co*-acrylamide) in eq. (4) shows a random distribution of NVP and PAM along the backbone, unless a special technique was employed to synthesize the polymer. It is also worth mentioning that the degree of hydrolysis, z, is limited according to the above structure.[12,17] Stahl[12] observed that NVP limited the level of AM hydrolysis, especially at high temperatures. They claimed that this copolymer increases the stability in the high-salinity, high-hardness, brine.

Table I gives the thermal behavior of PAM, PVP, and 71% HPAM-*co*-NVP, whose decomposition temperatures are illustrated in Figure 10. The TGA analyses show that the copolymers have significantly higher thermal stability than that of PAM by about 23°C, although the PVP itself has a lower T_d. Incorporation of the PVP with the hydrolyzed PAM increases the T_d significantly by more than 60°C. According to the bond dissociation energy, breaking the C—N linkage requires about 290 kJ mole^{-1}, making it weaker than the C—C bond (348 kJ mole^{-1}), C—O bond (351 kJ mole^{-1}), and C—H bond (391 kJ mole^{-1}). It is possible to state that thermal degradation proceeds easier through the breaking of the C—N bond than through the random scission of the C—C main chain. This degradation pathway could be justified by the release of pyrrolidone units as the main product of the initial step of the degradation pathway. Additionally, in the monomeric sequences along the polymeric backbone, the carbonyl oxygen of the pyrrolidone side ring is closer to the hydrogen atoms connected to the β-carbons of the main chain. These facts support a degradative mechanism[18] through the release of the pyrrolidone side groups as represented in Figure 11. It is anticipated that the copolymers synthesized in this research could be used as an EOR absorbent. Besides a high water-absorption ability (1100), the decomposition temperature is higher than 440°C. In oil-bearing formations, hydrocarbons are trapped under pressure in the pores of the rock matrix. The pressure and the temperature of an oil reservoir depends on the depth and the nature of the crude oil deposit in the reservoir. The pressure can vary from $1.4 \times 10^5 - 1.1 \times 10^7$ kg m^{-2}, and the temperature, from 25 to 150°C.[19]

CONCLUSION

Poly(1-vinyl-2-pyrrolidone-*co*-partially hydrolyzed acrylamide) was synthesized by γ-irradiation. Partially hydrolyzed polyacrylamide (HPAM) was first prepared by γ-irradiation through control of the total dose, dose rate, monomer concentration, and degree of sodium hydroxide hydrolysis. Important parameters of hydrolysis were varied to monitor the level of water absorption. The HPAM was then randomly copolymerized with 1-vinyl-2-pyrrolidone by γ-rays for several reaction parameters. The resulting random copolymer could absorb distilled deionized water of 1100 g g^{-1}. The amounts of appropriate total doses and dose rate for each polymerization step were recorded and their effects related to the material concentrations were discussed.
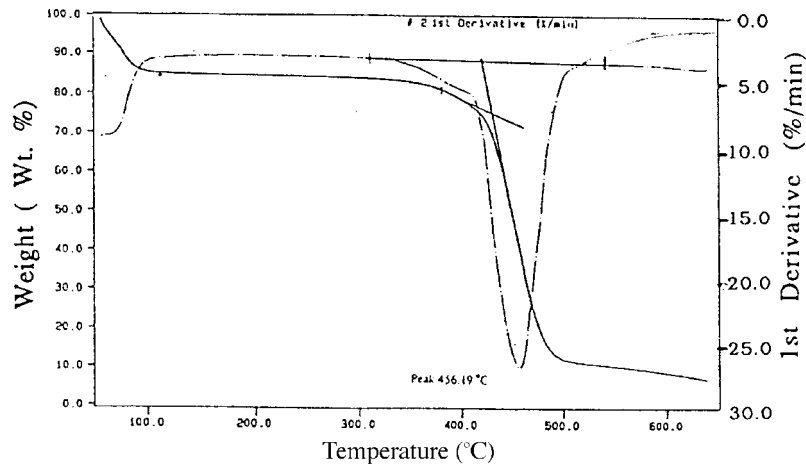
Table I   Decomposition Temperatures of PAM, PVP, HPAMs, and HPAM–NVPs

Type of Polymer		Decomposition Temperature (°C)
Homopolymer	Copolymer	
PAM	—	424
PVP	—	385
—	63% HPAM	391
—	71% HPAM	394
—	76% HPAM	388
—	80% HPAM	388
—	84% HPAM	385
—	63% HPAM-*co*-NVP	441
—	71% HPAM-*co*-NVP	447
—	76% HPAM-*co*-NVP	443
—	80% HPAM-*co*-NVP	440
—	84% HPAM-*co*-NVP	436
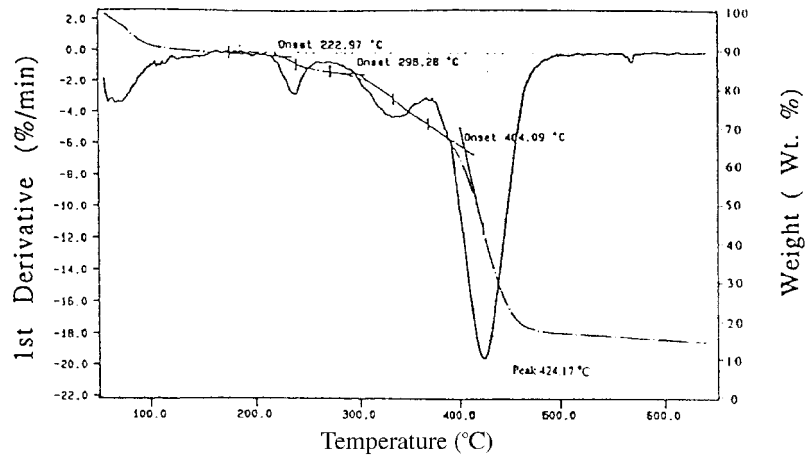
Thermogravimetric curve of PAM

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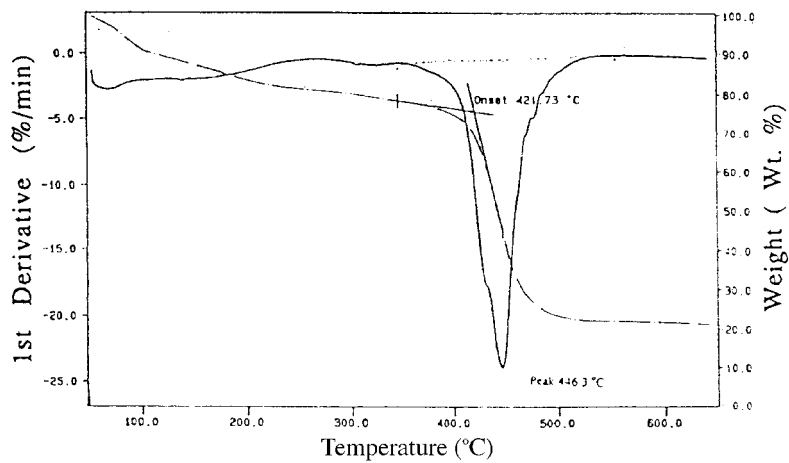
Thermogravimetric curve of 71% HPAM-co-PVP

Figure 10 Thermal behavior of PAM, PVP, and 71% hydrolyzed PAM-co-PVP.
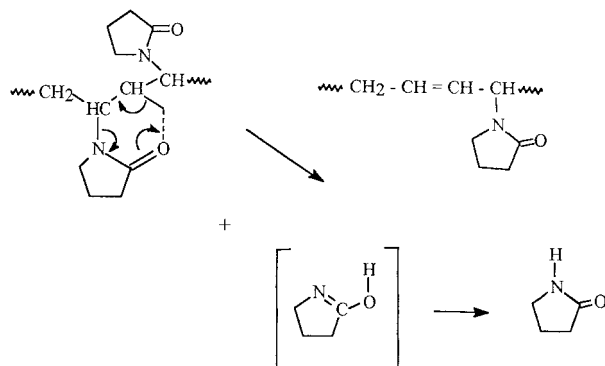
Figure 11 Degradation pathway of poly(*N*-vinylpyrrolidone) in the HPAM−PVP.

REFERENCES

1. S. Kiatkamjornwong and P. Suwanmala, in *Proceedings of the 5th International Conference on Radiation Curing: RadTech Asia'95 Symposium and Workshop,* Dec. 14–16, 1995, Chulalongkorn University, Bangkok, Thailand, Chaun Printing, Bangkok, 1995, pp. 329–339.

2. S. Kiatkamjornwong, J. Chvajarernpun, and C. Nakason, *Radiat. Phys. Chem.,* **42**, 47 (1993).

3. S. Kiatkamjornwong and P. Suwanmala, *Radiat. Phys. Chem.,* submitted.

4. G. Odian, *Principles of Polymerization,* 3rd ed., Wiley, Singapore, 1991, pp. 289–290.

5. J. E. Davis and E. Senogles, *Aust. J. Chem.,* **34,** 1413 (1981).

6. A. Chapiro, *Radiation Chemistry of Polymer Systems,* Interscience, New York, 1962, pp. 57–59.

7. P. A. Rey, in *Flocculation & Dewatering,* B. M. Moudgil and B. J. Scheiner, Eds., Engineering Foundation, New York, 1989, p. 195.

8. A. J. Swallow, *Radiation Chemistry of Organic Compounds,* Pergamon Press, Oxford, 1960, Chap. 6.

9. S. J. Guerruro, P. Boldareno, and J. A. Zurimendi, *J. Appl. Polym. Sci.,* **30,** 955 (1985).

10. I. G. Draganic and Z. D. Draganic, *The Radiation Chemistry of Water,* Academic Press, New York, 1971, pp. 38–42, 123–159.

11. G. D. Khune, L. G. Donaruma, M. J. Hatch, N. H. Klimer, S. Shepitka, and F. D. Martin, *J. Appl. Polym. Sci.,* **30,** 875 (1985).

12. G. A. Stahl and D. N. Schulz, Eds., *Water Soluble Polymers for Petroleum Recovery,* Plenum, New York, 1988.

13. C. Maltesh, P. Somassundaran, R. A. Kulkarni, and S. Gundiah, *Macromolecules,* **24,** 5770 (1991).

14. G. F. Fanta, E. B. Bagley, R. C. Burr, and W. M. Doane, *Starch / Starke,* **34,** 95 (1982).

15. S. B. Vitta, E. P. Stahel, and V. T. Stannett, *J. Appl. Polym. Sci.,* **32,** 5799 (1986).

16. A. Moradi-Araghi and P. H. Doe, Presented at the SPE 59th Annual Fall Conference, Houston, TX, September 16–19, 1984, SPE 13033.

17. K. Yasuda, K. Okajima, and K. Kamide, *Polym. J.,* **20**(3), 259 (1988).

18. C. Peniche, D. Zaldiver, M. Pazos, S. Paz, A. Bulay, and J. S. Roman, *J. Appl. Polym. Sci.,* **50,** 485 (1993).

19. I. Ahmed and A. Moradi-Araghi, *TRIP,* **2,** 92 (1994).