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AMIDOXIMATION AND CHARACTERIZATION OF NEW COMPLEXING HYDROGELS PREPARED FROM N-VINYL 2-PYRROLIDONE/ACRYLONITRILE SYSTEMS

Nurettin Sahiner^a; Nursel Pekel^a; Pinar Akkas^a; Olgun Güven^a

^a Department of Chemistry, Hacettepe University, Ankara, Turkey

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AMIDOXIMATION AND CHARACTERIZATION OF NEW COMPLEXING HYDROGELS PREPARED FROM N-VINYL 2-PYRROLIDONE/ ACRYLONITRILE SYSTEMS

Nurettin Sahiner, Nursel Pekel,* Pinar Akkas, and Olgun Güven

Department of Chemistry
Hacettepe University
Beytepe, 06532
Ankara, Turkey

Key Words: (N-vinyl 2-pyrrolidone, Acrylonitrile) Hydrogel, Gamma Rays, Amidoximation, Swelling

ABSTRACT

Solutions, obtained from the mixture of different mole ratios of N-vinyl 2-pyrrolidone and acrylonitrile, were irradiated in a ^{60}Co - γ source to produce copolymers. The swelling percentage curves were formed, and a diffusion exponent was calculated. For the uranyl ion adsorption, these copolymers were reacted with hydroxylamine hydrochloride to convert $\text{C}\equiv\text{N}$ groups to $-\text{C}=\text{N}-\text{OH}$ (amidoxime) groups. The optimum amidoximation time was determined by uranyl ion adsorption. The structure of copolymers, before and after amidoximation, was analyzed with spectroscopic and thermal methods.

*Author to whom correspondence should be addressed.

INTRODUCTION

To recover uranium from seawater or mining wastewaters, many different organic chelates are used [1-4]. Saraydyn *et al.* [5] and Karadad *et al.* [6] have prepared hydrogels containing acrylamide/maleic acid and acrylamide/itaconic acid for the uptake of uranyl ions from aqueous systems. The most widely used systems to adsorb uranyl ions from aqueous media are the amidoxime group containing polymeric systems. This group has been determined to show a strong affinity against uranyl ions. A number of papers however, have been published on radiation grafting of specific functional groups on PE hollow fibers and membranes to prepare flow-through systems for the removal of uranyl ions from sea water [7-9]. Amidoximated polymers are obtained by converting $C\equiv N$ groups to amidoxime groups in an organic media. Both amidoxime and hydrophilic groups containing adsorbents have a much higher uranium uptake than only amidoxime groups containing an adsorbent, because the amidoxime group is less hydrophilic among amide, carboxyl, and hydroxyl groups. From this point of view, interpenetrating polymer networks based on polyethylene glycol and acrylonitrile, have been synthesized and its adsorptive ability for uranium from aqueous media has been investigated [10].

There are relatively fewer studies related with hydrogels designed and synthesized for the uranyl ion adsorption from aqueous solutions [5, 6]. For the separation, in the use of chelating functional group containing hydrogels, some features of adsorbent such as durability, reuseability, and practical applicability are very important. In this aspect, hydrogels have some advantages over other systems. Recently, we [1, 11] prepared amidoxime containing interpenetrating polymer networks based on poly (N-vinyl 2-pyrrolidone/acrylonitrile) with γ -rays. In addition, we also synthesized amidoxime containing hydrogel prepared from N-vinylimidazole/acrylonitrile copolymers for the adsorption of uranyl ion from aqueous solutions [12, 13].

Herein, we report that hydrogels obtained with the irradiation of mixture of different mole ratios of N-vinyl 2-pyrrolidone (VP) and acrylonitrile (AN) in ^{60}Co - γ source. The swelling behavior of copolymeric hydrogels was investigated and the conversion of $C\equiv N$ groups to amidoxime groups in hydroxylamine hydrochloride-sodium hydroxide medium was conducted. The structural differences, before and after the amidoximation reaction, were investigated with FT-IR and TGA methods.

EXPERIMENTAL

Materials and Copolymer Synthesis

N-vinyl 2-pyrrolidone (VP) and acrylonitrile (AN), the products of Merck, were used for the preparation of crosslinked copolymers. Hydroxylamine hydrochloride, ($\text{NH}_2\text{OH}\cdot\text{HCl}$), and sodium hydroxide were supplied by Fisher and Merck firms, respectively.

VP was mixed with AN in different mole ratios (AN:VP, 0.67:1.00, 1.00:1.00, 1.50:1.00, and 2.00:1.00) and their binary mixtures were placed in PVC straws of 3mm diameter and irradiated at different doses in air at room temperature in a ^{60}Co Gammacell 220 irradiator at a fixed dose rate of 0.45 kGy/h. To remove the unreacted monomers and soluble fractions, irradiated mixtures were extracted with dimethyl formamide and water. Swelling experiments were done and diffusion exponent was calculated to explain the rate of water uptake into the gel.

Amidoximation Process and Conversion of Nitrile Group in PAN

Poly(N-vinyl 2-pyrrolidone/acrylonitrile) copolymeric hydrogels obtained in long cylindrical shapes were cut into pieces of 4-5 mm in length, swollen in aqueous medium and reacted with 0.05M hydroxylamine hydrochloride solution (1:1 in $\text{NH}_2\text{OH}\cdot\text{HCl}$: NaOH) at various temperatures. During the amidoximation reaction, samples were taken occasionally from the reaction medium, washed with distilled water, and then dried at room temperature. The conversion to amidoxime structure was determined by measuring the uranyl ion, UO_2^{2+} , adsorption capacity. The schematic formula for the reaction of hydroxylamine with the nitrile group in AN is shown as follows:

Optimum amidoximation conditions were determined by following the uranyl ion adsorption capacity of the amidoximated copolymers ($\text{g UO}_2^{2+}/\text{g dry resin}$) as a function of amidoximation reaction parameters. Optimum amidoximation conditions are determined as 50 hours of amidoximation time and 50C of temperature. The results obtained for different temperatures and different mole ratios are given in detail in another paper [14].

Swelling Studies

The swelling degree (%S) of hydrogels in distilled water before and after amidoximation was calculated from the following equation [15].

Here w_t is the weight of swollen gel at time t and w_0 is the weight of the dry gel at time 0.

Characterization (FT-IR and Thermal Analysis Methods)

Hydrogels were cut into fine pieces and dried in vacuum, then pressed into a pellet with KBr. The infrared absorption spectra of hydrogels were obtained by using a Nicolet 520 model FT-IR Spectrophotometer. The thermal characterization was performed by using a Du Pont 951 model Thermogravimetric Analyzer (TGA).

RESULTS AND DISCUSSION

Copolymeric hydrogels were obtained by irradiating the binary mixtures of different mole ratios of AN and VP. To determine the gelation of AN/VP solutions at different doses, first, hydrogels were dried in air and a vacuum oven, and then weighed. Later, hydrogels were transferred into dimethyl formamide and water for the extraction of soluble part of copolymer, respectively, then dried and weighed again. The gelation percentage was calculated from an insoluble network weight/total weight of copolymer ratio. 95 percent gelation (maximum percentage) has been reached at around 15 kGy dose [16]. The composition of hydrogels in feed and in extracted crosslinked structure was given in Table 1. The optimum amidoximation time for all copolymeric systems prepared by irradiation at 15kGy were found as 50 hours at 50C [14]. Swelling degree and diffu-

TABLE 1. The Composition of Hydrogels in Feed and in Extracted Crosslinked Structure

Feed Composition of Poly(AN/VP) Hydrogels (by mole)*	After Extraction, Composition of Poly (AN/VP) Hydrogels (by mole)
0.67:1.00	1.00:1.00
1.00:1.00	1.66:1.00
1.50:1.00	3.00:1.00
2.00:1.00	5.25:1.00

*Compositions given in the text

sion parameter, “n”, were calculated for amidoximated hydrogels. Figures 1 and 2 show a swelling degree of different compositions of copolymeric hydrogels, before and after amidoximation reaction. These figures show a swelling degree values decrease with the increase in the amount of AN in the composition of hydrogels. Since AN is hydrophobic, there is no interaction with water. Thus, the increase for AN in the composition of hydrogels results in a decrease in the swelling degree. Unlike AN, VP is a hydrophilic monomer and the increase for VP in composition of hydrogels cause an increase in the swelling. As shown in Figure 2, after amidoximation reaction hydrogels become more hydrophilic resulting in higher swelling degrees. The mole fractions of AN in hydrogels, after and before the amidoximation reaction, versus swelling degree values were plotted (Figure 3). As can be seen from the figure, swelling degree values decrease with an increase in AN mole fraction. This decrease is sharp and approximates to a constant value for poly (AN/VP) hydrogels, while the decrease in equilibrium swelling degree for amidoximated poly (AN/VP) is very steep. This can be interpreted as the decrease in swelling values and conversion of nitrile groups to amidoxime groups with the increase in the hydrophilicity of the structure. Furthermore, the swelling property of poly (AN/VP) hydrogels is determined by only the VP component, while the swelling of amidoximated of poly (AN/VP) hydrogels is based upon both VP and amidoxime groups. For this reason, amidoximated poly (AN/VP) hydrogel swell to higher values and just slows with the

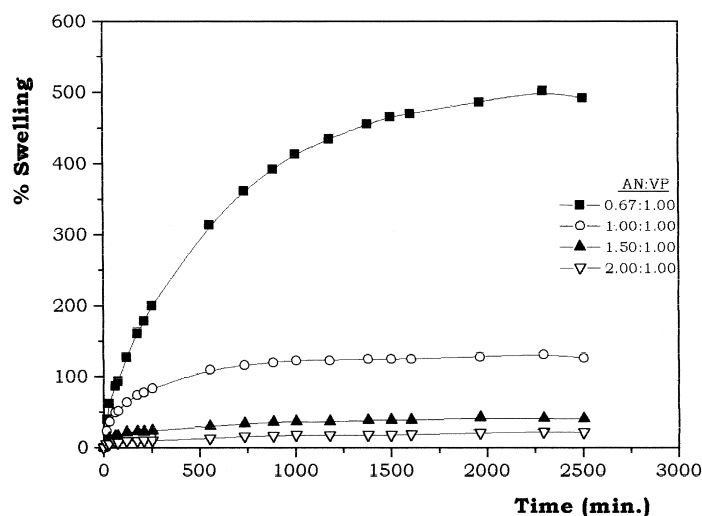


Figure 1. Swelling curves of different compositions of poly (AN/VP) hydrogels.

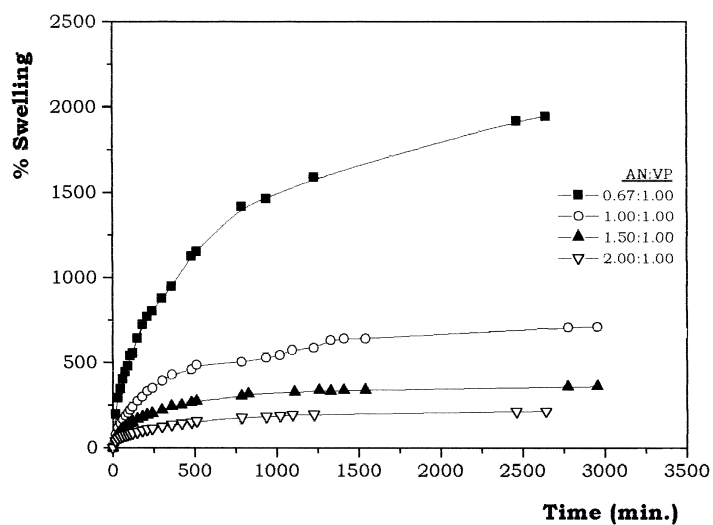


Figure 2. Swelling curves of different compositions of amidoximated poly(AN/VP) hydrogels.

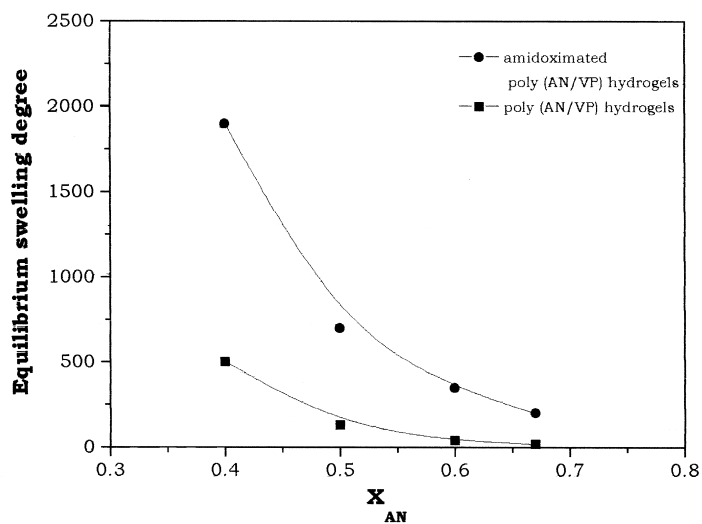


Figure 3. Changing of swelling percent values with mole fraction of AN in hydrogels.

TABLE 2. Changing of Diffusion Exponent, n , with Different Composition of Poly (AN/VP Hydrogels, Before and After Amidoximation

AN:VP Mole Ratio	XAN	n Before Amidoximation	n After Amidoximation
0.67:1.00	0.40	0.55	0.50
1.00:1.00	0.50	0.45	0.53
1.50:1.00	0.60	0.39	0.49
2.00:1.00	0.66	0.29	0.38

increase in AN content. Table 2 shows the diffusion exponent, “ n ”, of both hydrogels. “ n ” can be used to relate the time dependence on the water uptake rate. From this table, the “ n ” for both hydrogels decrease with the increase of AN content. Barr-Howell and Peppas [17] reported that the increase of swelling degree of PS in different solvent caused by the decrease in crosslinking density resulting in an increase in the molecular weight between crosslinks (M_c). When we compare same compositions for unamidoximated and amidoximated hydrogels, the swelling degree values are increased although M_c is constant resulting in an increase in “ n ”. This can be explained with the relaxation rate of polymer matrix. Polymer relaxation does not affect transport in Fickian diffusion ($n=0.5$), whereas relaxation processes become rate limiting with Case II transport ($n=1.0$). Both diffusion and relaxation affect transport in the anomalous regime ($0.5 < n < 1.0$).

As seen from the swelling curves, unamidoximated hydrogels reach the equilibrium swelling degree faster than the amidoximated hydrogels. With amidoximation reaction, only hydrophobic $C\equiv N$ groups were converted to the hydrophilic amidoxime groups. In other words, for the same composition there is no change in crosslinking density or/and molecular weight between crosslinks. The reason for the increase in “ n ” for same compositions is the increase of hydrophilicity of the structure.

The spectroscopic analysis of newly obtained structure was done with FT-IR spectrophotometer. Figure 4 shows the spectra of pure (a) polyacrylonitrile, (b) PVP, and (c) 1.00:1.00 mole ratio of poly (AN:VP) hydrogel. This figure, at 2235 cm^{-1} , a sharp characteristic band of $C\equiv N$ belonging polyacrylonitrile, and the peaks at 1650 cm^{-1} and 3500 cm^{-1} belonging to $C=O$ stretching vibration for PVP and OH stretching vibration, respectively. The broad band

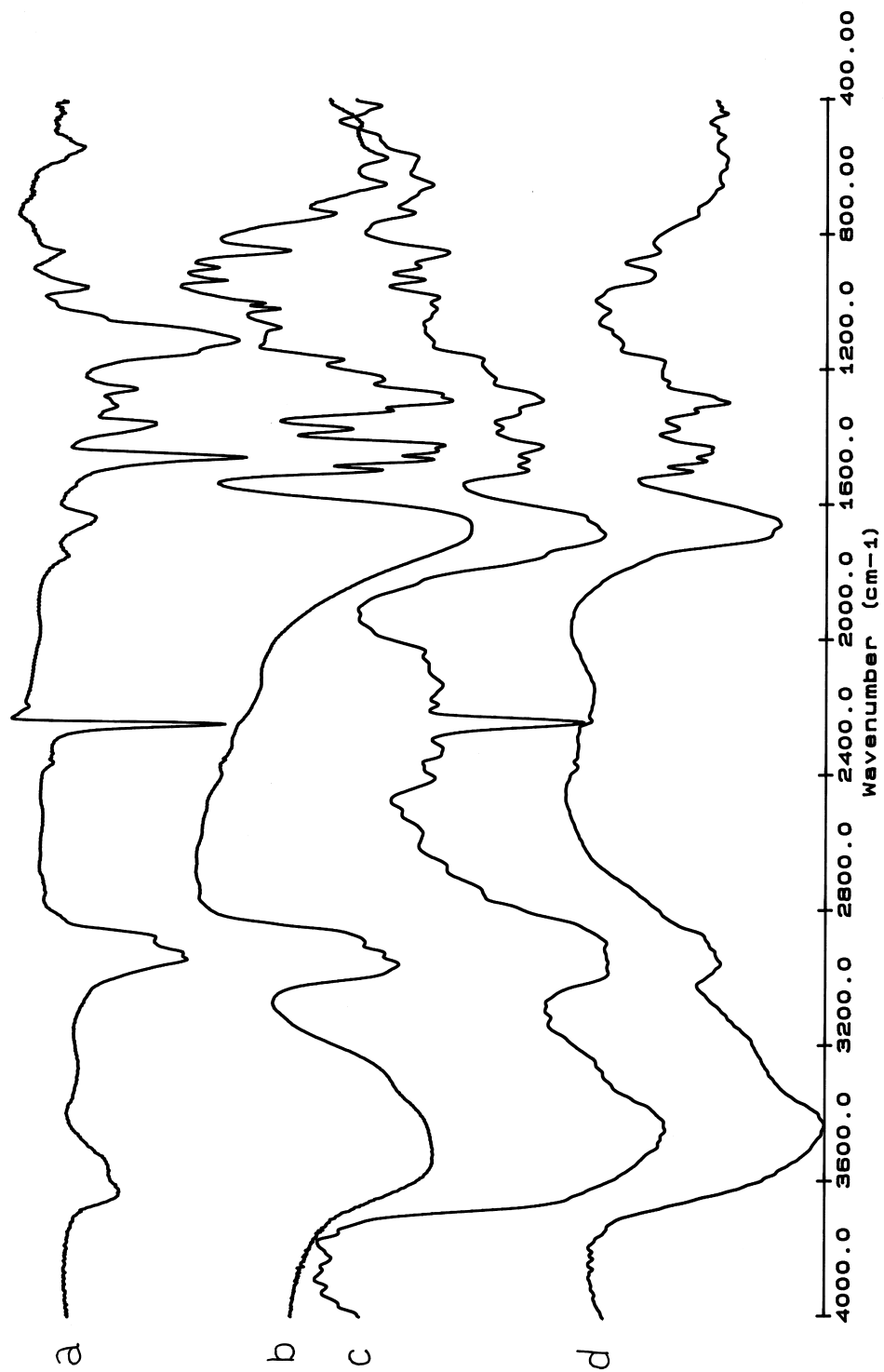


Figure 4. FT-IR spectra of (a) polyacrylonitrile, (b) PVP, (c) 1.00:1.00 mole ratio of poly (AN/VP) hydrogel, and (d) 1.00:1.00 mole ratio of amidoximated poly (AN/VP) hydrogel.

around 3500 cm^{-1} is possibly the hydroscopic feature of PVP. In Figure 4c, the characteristic bands of both components can be seen. Figure 4d shows FT-IR spectrum of the 1.00:1.00 mole ratio of amidoximated poly (AN:VP) hydrogel. It is important to note that the band intensity at 2235 cm^{-1} for $\text{C}\equiv\text{N}$ vibrational stretching decreased significantly with amidoximation time. When both spectra are compared to each other, for the amidoximated gels there is an increase in band intensity around 1650 cm^{-1} due to the newly formed $\text{C}=\text{N}$ groups, and a new band around 915 cm^{-1} belonging to N-O, vibrations can be seen. In addition, band broadening can be seen between $3500\text{-}2600\text{ cm}^{-1}$ for O-H and N-H bands due to the increase in the hydrophilicity of the structure with amidoximation reaction.

Thermal analysis of both unamidoximated and amidoximated hydrogel were conducted with TGA. Figure 5 shows the pure PAN thermogram. It can be seen from this thermogram that only 35% of PAN degraded heating up to 600C . The reason for this is the ring formation between $\text{C}\equiv\text{N}$ groups, which leads to very high thermal stability. For the pure PVP thermogram, Figure 6, there is characteristic single step degradation with maximum at 458C , and 95% of a weight loss is observed upon thermal degradation. In Figures 7 and 8, the TGA thermograms of 0.67:1.00 and 2.00:1.00 of AN:VP unamidoximated and amidoximated hydrogels can be seen. The thermograms, which are taken before the amidoximation reaction, show only one degradation temperature that is in between the degradations of pure components. When all thermograms, which were taken before amidoximation, (1.00:1.00 and 1.50:1.00 composition of AN:VP hydrogels' was not given) are compared before amidoximation reaction, the degradation temperatures shift toward the pure PAN degradation with the increase for AN component of hydrogels. By the modification of copolymeric hydrogels with amidoximation reaction, there are new degradation temperatures at lower temperature due to the newly formed amidoxime groups. Furthermore, the conversion of nitrile groups, which are thermally more stable, to amidoxime groups result in lower degradation temperature. TGA results confirm the random copolymerization of VP and AN.

CONCLUSION

(N-vinyl 2-pyrrolidone/acrylonitrile) hydrogels were prepared by γ -irradiating of binary mixtures of N-vinyl 2-pyrrolidone and acrylonitrile. $\text{-C}\equiv\text{N}$

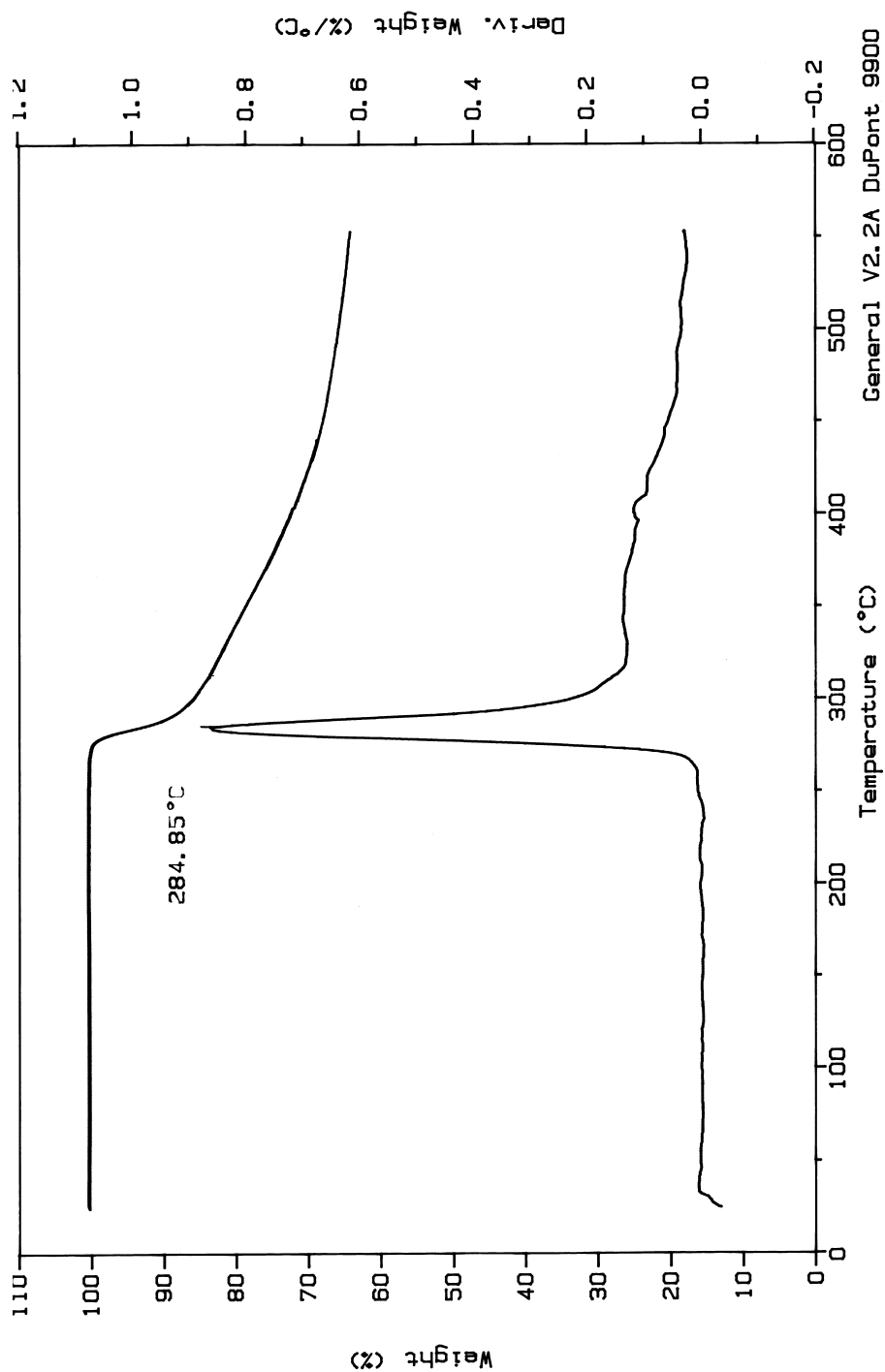


Figure 5. TGA thermogram of pure polyacrylonitrile.

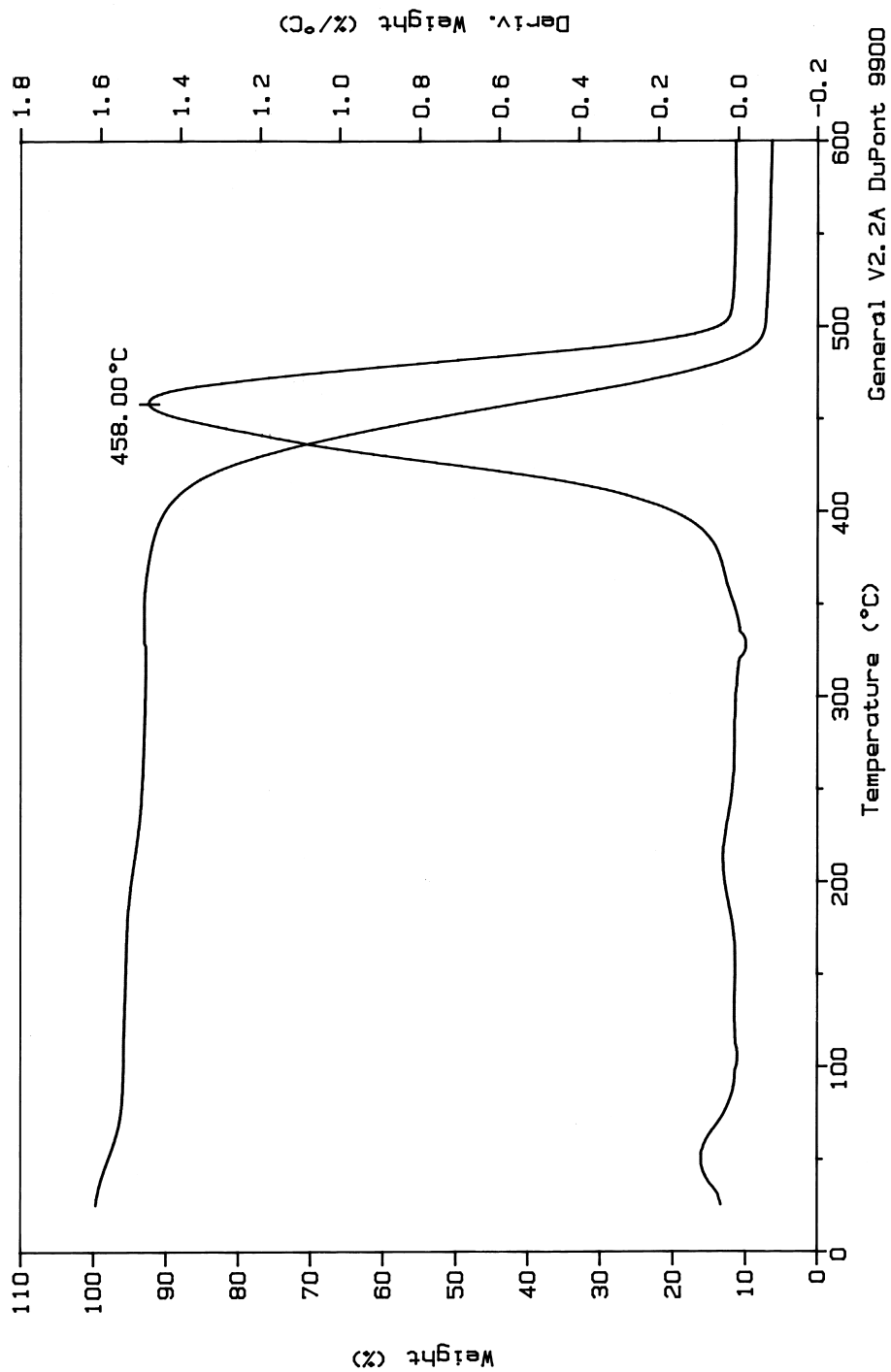


Figure 6. TGA thermogram of pure PVP.

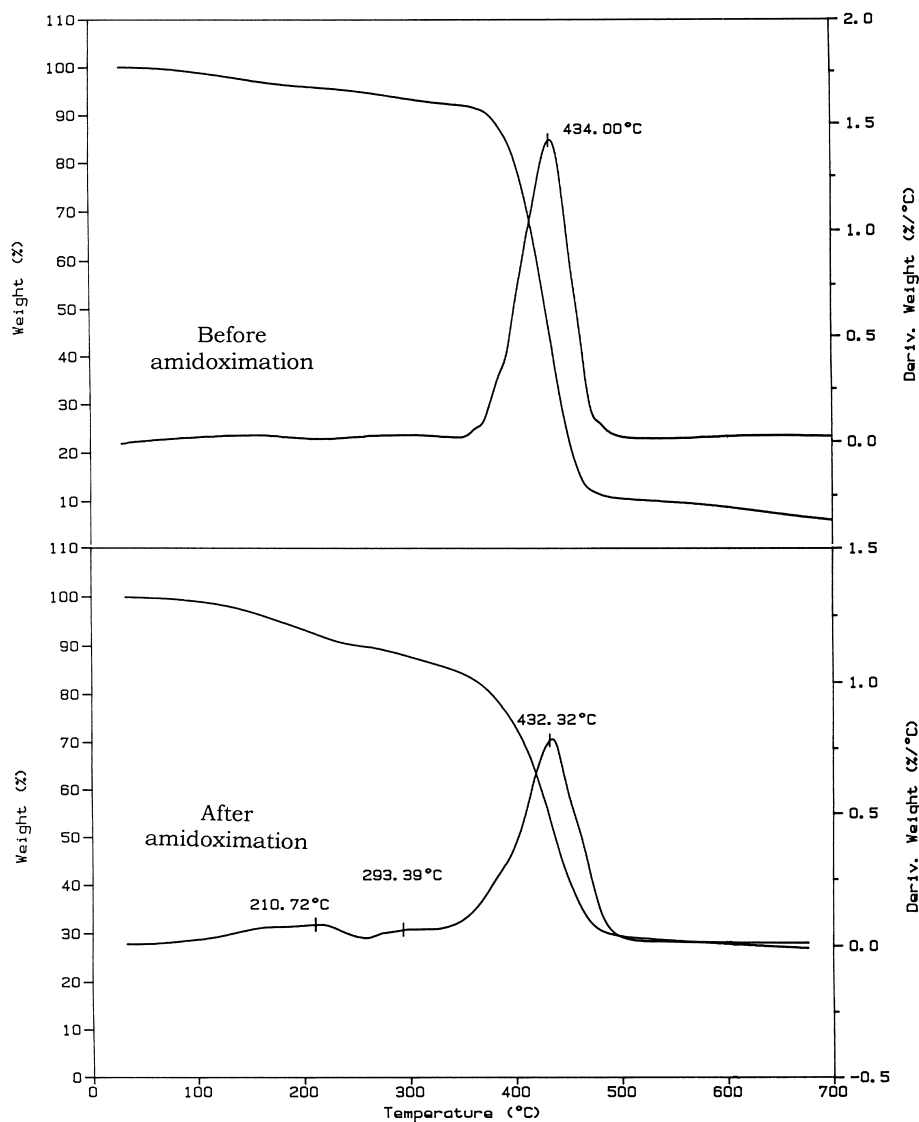


Figure 7. TGA thermograms of 0.67:1.00 mole ratio of poly (AN/VP) hydrogel before and after amidoximation.

groups in hydrogel were converted into $-C=N-OH$ groups in $NHOH.HCl/NaOH$ containing aqueous media. Hydrogels had 500 percent of swelling originally, this ratio reached 2000 percent of swelling after the amidoximation procedure. Hydrogels were characterized by using thermal and spectroscopic methods before and after amidoximation.

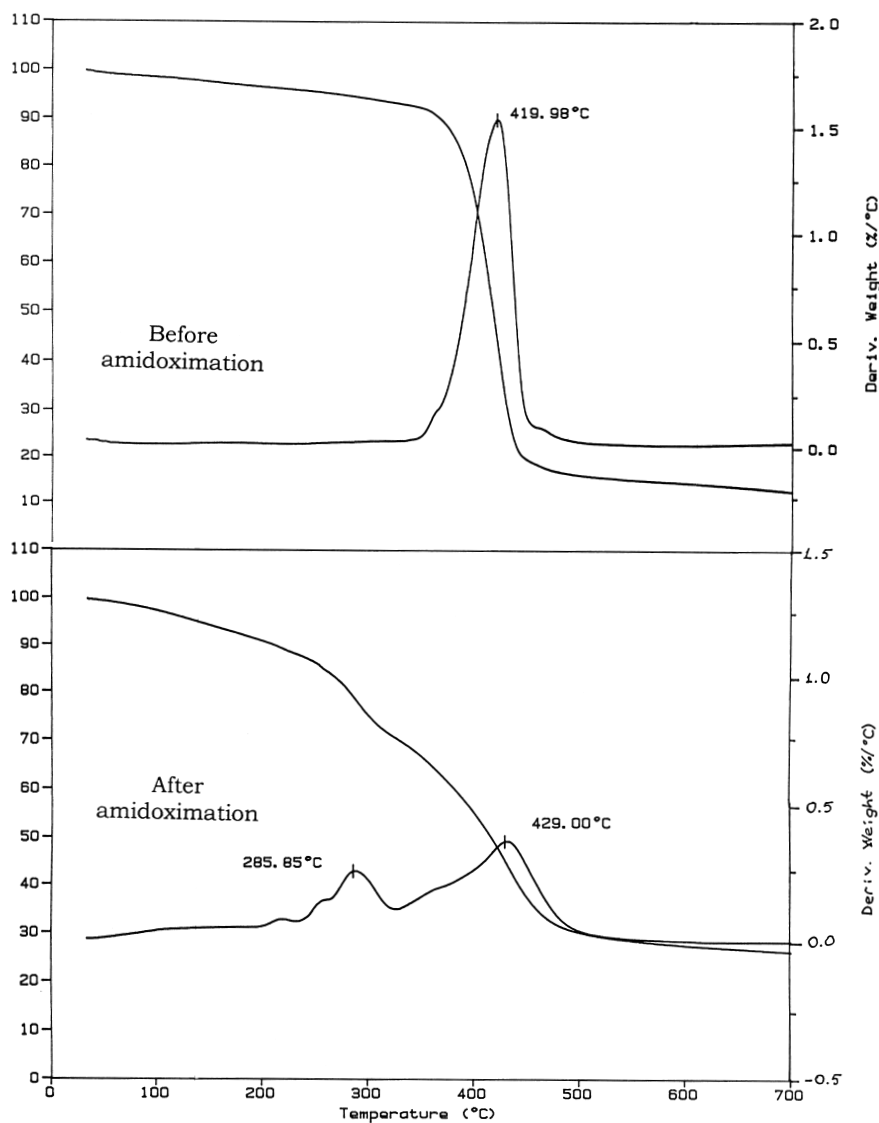


Figure 8. TGA thermograms of 2.00:1.00 mole ratio of poly (AN/VP) hydrogel before and after amidoximation.

As a result, in this study, hydrogels were investigated by way of some features such as swelling, spectroscopic and thermal behavior and it was shown that (N-vinyl 2-pyrrolidone/acrylonitrile) hydrogels could be used as a sorbent for the separation of uranyl ions in aqueous solutions.

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