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Development of new chelating hydrogels based on N-vinyl imidazole and acrylonitrile

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Abstract

Copolymers derived from the binary mixture of N-vinyl imidazole (VIm) and Acrylonitrile (AN) monomers have been synthesized by the irradiation of their solution with 60 Co- γ rays. Gelation percent–dose graphs were formed, and 80% of gelation (maximum percentage) has been reached at around 14 kGy dose. To impart metal ion adsorption properties, the hydrogels were amidoximated by the reaction of cyano groups on AN with hydroxylamine in aqueous media. Swelling behaviors of hydrogels were investigated before and after amidoximation. Hydrogels had 54% of swelling originally, this ratio reached 220% of swelling after amidoximation. The degree of amidoximation was followed by FT-IR spectroscopy. The structures of copolymers were analyzed spectroscopically and thermally before and after the amidoximation reaction. \bigcirc 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(N-vinyl imidazole/acrylonitrile); Amidoximation; y-rays; FT-IR spectroscopy

1. Introduction

It is very well known that chelating resins (Okamoto et al., 1985; Egawa et al., 1990; Kato et al., 1990) containing amidoxime groups show high selectivity toward uranium ion in aqueous media. Chelating resins and water-soluble chelating polymers have been used for the selective removal and recovery of heavy metal ions from drinking water and industrial wastewaters. For the purpose of uranium recovery from natural sea water, amidoxime containing porous chelating resins have been prepared from acrylonitrile with a variety of comonomer using different techniques by many researchers (Saito et al., 1990; Kubota and Shigehisa, 1995). These resins are synthesized through the reaction of acrylic resins and hydroxylamine. Kabay and Egawa (1993, 1994) have synthesized amidoxime containing resins by grafting acrylonitrile on polyethylene hollow fiber for the removal of uranyl ions from sea water. Güler et al. (1997) have prepared amidoxime containing interpene-

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trating polymer networks based on polyethylene glycol and acrylonitrile investigated its adsorptive ability for uranium from aqueous media.

Due to the large swelling capability, amidoximated polymers, however, often cause a dimensional instability when used in aqueous media. In order to recover significant amounts of uranium by adsorption method, the adsorbent should be contacted with a very large volume of seawater. On the other hand, hydrophilicity of adsorbent increases the adsorption capacity enhancing the amount of water to be contacted. In order to improve both stability of swelling resins and the easy access of the functional groups, amidoxime group containing resins (Sahiner et al., 1998, 1999, 2000; Pekel et al., 1999, 2000a, b) were synthesized by radiation grafting technique. Crosslinking, which is also caused by high-energy radiation plays an important role on controlling the swelling behaviors, consequently the adsorption ability for uranium.

In the present work, copolymers based on N-vinylimidazole (VIm) and acrylonitrile (AN) were synthesized by irradiation of their binary mixtures. Amidoximecontaining resins were prepared by the reaction of cyano group in AN with neutralized hydroxylamine hydrochloride. Copolymeric structure and properties were investigated. FT-IR and Thermal Analysis methods were used for characterization and amidoximation.

2. Experimental

2.1. Materials and copolymeric hydrogel synthesis

N-vinylimidazole (VIm) and acrylonitrile (AN), the products of Merck, were used, as received. Hydroxylamine hydrochloride and sodium hydroxide were supplied from Carlo Erba and Merck firms, respectively.

VIm was mixed with different mole ratios of AN, and the solutions were irradiated to different doses in PVC straws in 60 Co- γ source, Gammacell 220 in air at room temperature at a dose rate of 0.45 kGy/h. Feed compositions employed in the present work were 0.50:1.00, 0.75:1.00, 1.00:1.00, and 1.25:1.00 by mole AN: VIm. Hydrogels obtained in long cylindrical shapes were cut into pieces of 4–5 mm length and their percent of gelations to insoluble network was determined gravimetrically. Irradiated mixtures were immersed into dimethyl formamide to extract the unreacted monomers and uncrosslinked soluble fractions.

2.2. Amidoximation of nitrile group in poly (AN/VIm) hydrogels

The amidoximation reactions were conducted in aqueous medium of neutralized hydroxylamine hydrochloride solutions (mole ratio 1:1 in NH₂OH.HCl: NaOH) at 50°C. During the amidoximation reaction, samples taken from the reaction media at the predetermined time intervals, washed with distilled water, and dried in vacuum oven at 35°C. The conversion of nitrile groups to amidoxime was determined by following the changes in $C \equiv N$ band areas in AN from FT-IR spectra. The reaction of hydroxylamine with the nitrile group can be shown as follows:

$$HO-NH_{2} + C \equiv N \longrightarrow \begin{matrix} V \\ I \\ C \equiv N-OH \\ I \\ NH_{2} \end{matrix}$$

The percentage conversion of nitrile group in the structure was calculated using

$$C_n = \frac{A_0 - A_t}{A_0} \times 100,$$
 (1)

where C_n is the percent of conversion and A_0 and A_t are the areas of $C \equiv N$ band observed at 2200 cm⁻¹ before and after the amidoximation time *t*, respectively.

2.3. Swelling studies

The swelling degree (%S) of hydrogels in distilled water before and after amidoximation was calculated from the following relation (Peppas, 1986):

$$S(\%) = \frac{w_t - w_0}{w_0} \times 100,$$
(2)

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

2.4. Characterization (FT-IR and thermal analysis methods)

The samples while wet were cut into fine pieces, dried in vacuum, and pressed into pellets with KBr. The infrared spectra of samples were taken with Nicolet 520 model FT-IR spectrophotometer. The thermal characterization was performed using Du Pont 951 model Thermogravimetric Analyzer.

3. Results and discussion

The mixture of VIm with different mole ratios of AN were irradiated in γ source, and hydrogels were obtained. From the known values of Alfrey-Price parameters ($Q_2 = 0.11$, and $e_2 = -0.68$; Brandrup and Immergut, 1989), the constant of copolymerization for acrylonitrile (M_1) and N-vinylimidazole (M_2) pair were calculated to be $r_1 = 0.42$, and $r_2 = 0.062$. As evident from these values, random copolymerization is realized in the monomer system studied. Their percent of gelation-dose curves are shown in Fig. 1. It can be seen from this figure that the maximum gelation (about 80%) is reached approximately at 14 kGy dose irrespective of the initial composition. 14 kGy irradiated samples were



Fig. 1. Gelation percent-dose plot for poly (AN/VIm) hydrogel systems.

 Table 1

 The composition of hydrogels before and after extraction

Before extraction, composition of AN:VIm (by mole)	After extraction, composition of AN:VIm (by mole)
0.50:1.00	0.70:1.00
0.75:1.00	1.12:1.00
1.00:1.00	1.46:1.00
1.25:1.00	2.29:1.00

later used for swelling experiments. To determine the composition of hydrogels by mole of AN and VIm after irradiation, irradiated mixtures were immersed into water and dimethyl formamide, respectively, to extract the unreacted monomers and uncrosslinked soluble fractions. The composition of hydrogels after irradiation was calculated by using gravimetric measurements, and data are shown in Table 1.

Fig. 2 shows the dependence of swelling on the composition of the crosslinked copolymers of poly (AN/VIm). With increasing VIm content, the gels have shown increasing swelling degree. The highest swelling degree was found for AN : VIm copolymers of 0.70 : 1.00 molar ratio. The maximum gelation dose is reached about 158 kGy for bulk PVIm, and its swelling degree is 340. There is a substantial decrease in the swelling degree of PVIm hydrogel by the incorporation of AN into the copolymeric system. While there is no interaction with water for pure polyacrylonitrile (PAN), the presence of VIm imparts the swellability of copolymeric system in water. On the other hand, the increase in the amount of AN in the copolymeric system enhances the mechanical stability of copolymers. The hydrogels thus prepared



Fig. 2. Swelling degree curves for different mole ratios of poly (AN/VIm) hydrogel systems.

were later used to convert them into VIm/amidoxime structures. The amidoximation reaction was conducted at 50°C (Sahiner et al., 2000) in aqueous NH₂OH.HCl-NaOH medium. Samples taken from the reaction medium at pre-determined time intervals were washed and dried in vacuum oven. Their FT-IR spectra were taken, and some representative curves are given in Fig. 3. As can be seen from these spectra, the intensities of $C \equiv N$ bands in hydrogel decrease proportionally with the amidoximation reaction time. The relative decrease in the area of characteristic $C \equiv N$ bands in AN segments in hydrogels was plotted versus amidoximation time, and the time that required for maximum amidoximation was determined as 50 h. In addition, percentage amidoximation conversion (C_n) was calculated using Eq. (1).

Fig. 4 shows the progress in percentage amidoximation with the amidoximation reaction time for all compositions of AN: VIm copolymers. In general, the amidoximation increases with the increase in the reaction time. For the mole ratio of 2.29:1.00 (AN: VIm), 69% amidoximation was found which is lesser than the values of 1.46:1.00 and 1.12:1.00 systems. Hydrophilicity of the system decreases with the increase in the amount of AN. Since the conversion reaction has been carried out in aqueous medium, the diffusion of NH₂OH into the structure becomes more difficult with the increase in the amount of AN in the polymeric systems. These results are consistent with the swelling experiments that were conducted after amidoximation reactions. Table 2 shows the swelling degree before and after amidoximation. There is a decrease in swelling degree values with the increase in the amount of AN content of the systems before and after amidoximation. Swelling degree values were compared for the same composition of hydrogel, swelling degree increased after amidoximation reaction due to the change in the structure of $-C \equiv N$ groups to $H_2N-C = N-OH$ groups. In other words, nitrile groups, which are hydrophobic, converted to hydrophilic amidoxime groups. Similar results were obtained with the study of poly (acrylonitrile/N-vinyl 2-pyrrolidone) hydrogel systems (Sahiner et al., 2000).

Fig. 5 shows the FT-IR spectra of 1.46:1.00 mole ratio of AN:VIm copolymers before and after the amidoximation reaction. The peaks shown in Fig. 5(c) can be analyzed as follows.

At 2200 cm⁻¹ illustrate the characteristic band of $C \equiv N$ groups in PAN, 3110 cm⁻¹, the C–H stretching vibration band in PVIm ring, and 1670 cm⁻¹, the possible N–H stretching vibration in PVIm ring, 1500 cm⁻¹, the characteristic C–N stretching vibrations, and 744 cm⁻¹, C–H ring bending vibrations of PVIm ring. In the FT-IR spectra, taken after amidoximation reaction, Fig. 5(d), there are some differences due to the newly formed H₂N–C=N–OH groups. The broad peak



Fig. 3. FT-IR spectra of amidoximated poly (AN/VIm) hydrogels with reaction time (h), (a) O, (b) 1.25, (c) 5, (d) 14, (e) 18, (f) 37, (g) 55.



Fig. 4. The change in the relative intensity of $C \equiv N$ band with reaction time.

at 2400–3800 cm⁻¹ can be attributed to H-bondings for NH₂ and O–H in the amidoxime structure. The characteristic bands at 1600 and 900 cm⁻¹ belong to C=N and N–O stretching vibrations, respectively. In Fig. 5(d), the peak at 2200 cm⁻¹ gets smaller with amidoximation reaction, but does not completely disappear. Depending upon the increase in the amount

Table 2 Percent swelling equilibrium values of hydrogels before and after amidoximation

Composition of AN:VIm (by mole)	Before amidoximation, % swelling value	After amidoximation, % swelling value
0.70:1.00	54	220
1.12:1.00	47	165
1.46:1.00	44	107
2.29:1.00	32	71

of AN in the copolymeric system, the hydrophobicity of system increases. Therefore, the diffusion of NH_2OH to the structure gets harder resulting in incompletion of conversion of $C \equiv N$ groups to amidoxime groups in the inner sides of the copolymer.

The thermal analysis of copolymeric systems was carried out by using thermogravimetric analyser (TGA) for pre/post-amidoximation reaction. In order to observe copolymeric hydrogels' thermal behavior, hydrogels were ground into fine pieces and its thermogravimetric analysis (TGA) was performed in an N₂



Fig. 5. FT-IR spectra of (a) pure PAN, (b) pure PVIm, (c) poly (AN/VIm) hydrogel, (d) amidoximated poly (AN/VIm) hydrogel.







Fig. 7. TGA thermogram of amidoximated 1.46:1.00 mole ratio of poly (AN/VIm) hydrogel.

atmosphere. Figs. 6 and 7 show the thermograms for the mole ratio of 1.46:1.00 copolymeric hydrogel before and after amidoximation. The decomposition temperature for pure PAN is 285°C (Sahiner et al., 1999), and for pure PVIm is 459°C. When their pure samples were heated up to 600°C, the weight loss for pure PVIm was almost 100%, while the weight loss for pure PAN was 35%. This result was explained as the formation of ring structure among the $C \equiv N$ groups of PAN resulting in an increase in the thermal stability of the structure. In Fig. 6, on the derivative curve of this thermogram instead of two separate decomposition temperatures, there is only one broad decomposition temperature seen at around 382°C, which is between the decomposition temperatures of the two constituent polymers. Absence of a sharp peak in the derivative thermogram at 285°C indicates that AN moieties in the copolymer structure are not present in blocks or in segments and rather distributed randomly on the main chain. Thermograms, taken for the other compositions, show very similar results. Moreover, they showed a shift towards the pure PAN decomposition temperature with the increase in the amounts of AN contents in the copolymeric systems. Fig. 7 shows TGA thermogram of amidoximated copolymer analyzed in Fig. 6. Due to the newly formed $H_2N-C = N-OH$ groups and remaining unconverted groups and resulting complex structure, the

thermogram shows multiple decomposition temperatures. It is highly probable that at 208°C amidoxime structures start lossing weight, and the decomposition temperature for $C \equiv N$ groups at 272°C is still seen while new decomposition temperatures at 351 and 424°C are also observed.

4. Conclusion

Poly (acrylonitrile/N-vinylimidazole) hydrogels have been prepared as random copolymer crosslinked by radiation. AN moieties of these gels have been converted into amidoxime structures with high conversion efficiencies. The maximum gelation dose has been reached at about 14kGy dose. Swelling degree decrease with the increase in the amount of AN in copolymeric system before and after the amidoximation reaction. From the FT-IR evaluation, the conversion of nitrile groups to amidoxime groups has been observed to decrease as the content of AN increased in the structure. The random copolymeric structure of the gels has been proved by thermogravimetric analysis of homo and copolymers. The amidoximated structures show good swelling properties in aqueous systems. They are considered as potential adsorbents for uranyl and heavy metal ions from aqueous systems.

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