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Preparation of modified polyacrylamide hydrogels and application in removal of Cu(II) ion

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Abstract

Modified polyacrylamide hydrogels were prepared by transamidation and Hofmann reactions using different amine compounds. Products were characterized by their amine value (AV), equilibrium degree of swelling (EDS) and FT-IR spectroscopy. In case of transamidation on crosslinked polyacrylamide (CPAAm) in aqueous media, AV increased with reaction time and temperature, but EDS decreased with time, especially for reactions at higher temperatures. On the other hand, transamidation reactions on linear polyacrylamide (LPAAm) gave products with higher AV, but quite lower EDS than aqueous media products. Hofmann reactions were carried out on CPAAm with different amounts of NaOCl in the presence of amine compounds, to yield products with higher AV and EDS compared with conventional Hofmann reactions. The products were used for removal of copper (II) ion at pH = 5.5 by batch equilibrium technique. A maximum removal capacity of 2.93 mmol Cu(II)/g was obtained after a regeneration cycle. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Modified polyacrylamide; Hydrogel; Transamidation

1. Introduction

In recent years, the synthesis of crosslinked polymers with chelating groups have received considerable attention for rapid and inexpensive metal-ion separation and concentration [1,2]. Ionic derivatives of polyacrylamide can also be used for this purpose. They can be obtained by copolymerization of different functional monomers or by the modification of amide group in the polymer matrix, which is partially accessible for chemical transformation. In previous works, modified polyacrylamides have been obtained from linear polyacrylamides by various modification reactions such as Mannich [3], Hofmann [4,5] or by copolymerization of different functional monomers, such as diallyldimethylamonium chloride, dimethylaminoethylmethacrylate, 2-acrylamido propanesulphonic acid, 3-acrylamido-3-methylbutanoic acid [6–9]. Modified polyacrylamide was also obtained by the polymerization of acrylamide with different crosslinking agents, followed by the reaction with ethylenediamine (EDA) in nonaqueous media, to obtain poly(*N*-2-aminoethylacrylamide) [10–12].

In this work, transamidation reaction was carried out on crosslinked polyacrylamide (CPAAm) in aqueous media and on linear polyacrylamide (LPAAm) in nonaqueous media, using EDA, diethylenetriamine (DETA) and triethylenetetramine (TETA), for the first time. Hofmann reaction was also carried out on CPAAm in the presence of EDA, DETA, also for the first time. The modified crosslinked polymers were characterized and used as chelating agents for removal of copper (II) ion.

2. Experimental

2.1. Materials

Acrylamide (AAm) and *N*,*N'*-methylenebisacrylamide (NMBA) monomers were Merck ‘for synthesis’, all of the other reagents used were ‘extra pure’ chemicals. LPAAm had a viscosity average molecular weight of 2,300,000 ($\bar{M}_v$) (American Cyanamid). Technical grade NaOCl ~5.0% (w/w) was used for the Hofmann reaction. Bidistilled water for polymerization reactions and distilled water for modification reactions was used.

2.2. Instruments

The FT-IR spectra were obtained by Perkin Elmer, Spectrum GX model instrument with ATR technique. The copper(II) ion was determined by atomic absorption

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spectrometry using Varian Spectro AA 220-FS atomic absorption spectrometer.

2.3. Preparation of CPAAm

CPAAm was prepared by free radical polymerization of AAm monomer and NMBA crosslinking agent. Reactions were carried out in a 1 l, five necked glass reaction vessel equipped with a mechanical stirrer, reflux condenser, thermometer and N_2 gas inlet. The dissolved oxygen was removed by bubbling purified nitrogen gas for 30 min through water (450 ml) at room temperature before AAm (50 g) and NMBA (0.5 g) addition. The reaction mixture was heated to 50°C and $K_2S_2O_8$ (0.15 g) and $KHSO_3$ (0.15 g) as initiator couple was added with stirring, and the reaction was continued for 5 min. The obtained gel was disintegrated in a blender, washed with water and methanol, filtered and dried to constant weight at 30°C under vacuum to give a white, fine powder. The yield of reaction was determined from the amount of free monomer residue [13].

2.4. Transamidation reaction of CPAAm in aqueous media

The transamidation reaction of CPAAm was carried out in reaction system described above, with different amine compounds. CPAAm was swollen in water at ambient temperature for 1.5 h and then EDA or DETA (36% (w/w) aqueous solution) was added to provide $r = 1/3.2$ and 1/12 ($r =$ the molar ratio of AAm to amine compound). Reactions were carried out at 50 and 90°C for 3 and 9 h. The reaction was also carried out with DETA ($r = 1/12$) at 90°C for 9 h. The gels were disintegrated in methanol in a blender, filtered and washed with distilled water until the filtrate was free from amine, as determined by color reaction with ninhydrine [14] and then washed with methanol and dried to constant weight under vacuum at 30°C, to give white fine powders.

2.5. Transamidation reaction of LPAAm in nonaqueous media

Amine compound (EDA, DETA or TETA and $r = 1/12$) was placed in a round-bottom flask and the LPAAm was added with stirring, then heated to 90°C and kept at this temperature for 9 h. The reaction mixture was poured into excess methanol and filtered, then washed with methanol until free from amine, and dried to constant weight under vacuum at 30°C, to give white or yellowish powders.

2.6. Hofmann reaction of CPAAm

The reactions were carried out in the reaction system used in transamidation reactions of CPAAm. In the first part of these experiments, Hofmann reactions were carried out in conventional way [4] with different amounts of NaOCl (molar ratios of AAm/NaOCl were 1/0.3, 1/1 and 1/2). In the second part, the same reactions were carried out in the presence of EDA or DETA. CPAAm was swollen in water for 1.5 h and then EDA or DETA was added (in contrast to conventional Hofmann reaction where no amine is added) and stirred for 30 min at ambient temperature. Freshly prepared NaOH–NaOCl solution at 5°C was added and the reaction was continued at 20°C for 2 h. The reaction product was disintegrated in isopropyl alcohol in a blender, filtered and washed with distilled water until the filtrate was free from amine. Gels were washed with isopropyl alcohol again and dried to constant weight under vacuum at 30°C. The conventional Hofmann reaction gave the yellow and sticky products, but the other reactions carried out in the presence of amines gave white fine powders.

2.7. Determination of amine value

The polymers (50 mg) were swollen in distilled water (25 ml, neutralized against methylorange indicator) and titrated with HCl (0.1N) [10]. The results are given in Tables 1–3 as mmol/g dry polymer. (Since some of the polymers contained also carboxylate groups, one should keep in mind that ‘amine value’ in those cases should be accepted to be ‘total basic group value’.)

2.8. Determination of equilibrium degree of swelling

The polymers were swollen in distilled water for 4 days and the degree of swelling was determined gravimetrically. The amount of water adsorbed per gram dry polymer under equilibrium conditions is given in Tables 1–3 as EDS (%).

2.9. Determination of Cu(II) ion removal capacity

The polymers (50 mg) were added to copper (II) solution (0.01574 mol/l, 25 ml) which had pH of 5.5. The amount of residual metal in the solution was followed by atomic absorption spectrometry, up to 24 h. The results are given as mmol/g dry polymer in Tables 1–3. For comparison purposes, a polymer (TA8) was also added to Cu(II) solution which was acidified to pH 3.0 and 4.5 by HNO_3 addition.

Some polymers (TA8, TN1, TN2) were regenerated by treating the polymers with dilute HCl solution (0.1N) and the acid-treated polymers were washed with distilled water to remove unreacted HCl and neutralized with dilute NaOH (0.1N) and again washed with distilled water to remove excess NaOH before a second cycle. The Cu(II) ion removal capacities in case of these regenerated polymers were also determined.

3. Results and discussion

3.1. Preparation of CPAAm

The network structure of the polyacrylamide gels is highly dependent on the concentration of AAm and NMBA during polymerization [15,16]. The increase in the

Table 1
The conditions of transamidation reaction of CPAAm in aqueous media and the properties of modified polymers

Polymers	Amine	Molar ratio (AAm/amine)	Transamidation		AV (mmol/g)	EDS (%)	Cu(II) ion removal capacity (mmol/g)
			Temperature (°C)	Time (h)			
CPAAm	–	–	–	–	–	3280	2.7×10^{-2}
TA1	EDA	1/3.2	50	3	0.74	16,900	0.77
TA2	EDA	1/3.2	50	9	1.20	18,700	1.04
TA3	EDA	1/3.2	90	3	1.88	21,700	1.80
TA4	EDA	1/3.2	90	9	2.40	17,400	2.24
TA5	EDA	1/12	50	3	1.18	17,900	1.06
TA6	EDA	1/12	50	9	1.27	17,900	1.17
TA7	EDA	1/12	90	3	1.98	22,000	1.84
TA8	EDA	1/12	90	9	2.46	17,900	2.27
TA9	DETA	1/12	90	9	2.19	8750	1.99

amount of NMBA increases the crosslink density and rigidity of gels, and consequently, as expected the extent of swelling of the gels in water decreases. A CPAAm with high equilibrium degree of swelling (EDS), in comparison with those reported previously [11,12], was prepared by using a low amount of NMBA by solution polymerization of the monomers in water. The polyacrylamide gel had an EDS of 3280% and was obtained with a yield of 91.3%.

3.2. Transamidation reaction

The amino functionalized polyacrylamides has been obtained by transamidation reaction of polyacrylamide. In case of diamines, the possibility of transamidation reaction with the both amino groups of a diamine molecule leads to additional crosslinking, which in turn lowers the swelling of the polymers. But, crosslink density of the polymers could be reduced by employment of excess amount of amine [12].

The conditions of transamidation reactions of CPAAm and the properties of modified polymers are given in Table 1. The amine value (AV) of the polymers varied between 0.74 and 2.46 mmol/g and increased with reaction time and temperature, as well as the amount of amine used per mole of AAm. For example, increase in the reaction time from 3 to 9 h (TA1, TA2) increased the AV from 0.74 to 1.20 mmol/g. Increase in the reaction temperature was more effective (TA1, TA3) where AV increased from 0.74 to 1.88 for 3 h and from 1.20 to 2.40 mmol/g (TA2, TA4) for 9 h. Increasing the molar ratio from 1/3.2 to 1/12 provided modest increases in AV in all cases, indicating that reaction temperature was the dominant contributor to higher AV.

The EDS, in general, increased with the AV of the polymer, but especially at the higher reaction temperature of 90°C, increasing the reaction time decreased EDS due to crosslinking (TA3, TA4 and TA7, TA8). It is also known that larger amine molecules increase the crosslink density [11,17] and decrease EDS. This is confirmed in case of employment of DETA instead of EDA (TA9, TA8) where EDS decreased from 17900 to 8750%. The EDA transamidation products had 5–7 times higher EDS than that of the unmodified CPAAm.

Transamidation reactions of LPAAm were carried out by using EDA, DETA and TETA in nonaqueous media. Reaction conditions and properties of the polymers are given in Table 2. The reactions with EDA and DETA resulted in the crosslinked polymers (TN1 and TN2), but a partially water soluble polymer(TN3) was obtained in case of TETA. The products had higher AV, but quite lower EDS, as compared with the polymers prepared in aqueous media. TN1 and TN2 had high AV of 3.09 and 3.22 mmol/g, but their EDS were only 3950 and 2900%, respectively. This is due to the absence of ionizable groups on the polymer molecules. As will be discussed below, FT-IR spectra (Fig. 1) confirms that no carboxylate groups were formed in contrast with transamidation of CPAAm in aqueous media.

3.3. Hofmann reaction

The cationic derivatives of polyacrylamide can be obtained by Hofmann reaction [4] in the presence of

Table 2
The conditions of transamidation reaction of LPAAm in nonaqueous media and the properties of modified polymers

Polymers	Amine	Molar ratio (AAm/amine)	AV (mmol/g)	EDS (%)	Cu(II) ion removal capacity (mmol/g)
TN1	EDA	1/12	3.09	3950	2.08
TN2	DETA	1/12	3.22	2900	0.91
TN3[a]	TETA	1/12	2.86	–	–

[a] The EDS could not be determined due to partial solubility of polymer in water.

Table 3
The conditions of Hofmann reactions and the properties of modified polymers

Polymer	Amine	Molar ratio (AAm/amine/ NaOCl/NaOH)	AV (mmol/g)	EDS[a] (%)	Cu(II) ion removal capacity (mmol/g)
H1	–	1/0/0.3/0.323	1.26	1900	0.92
H2	–	1/0/1/0.323	0.68	1700	0.22
H3	EDA	1/12/0.3/0.323	1.32	7750	1.03
H4	EDA	1/12/1/0.323	1.91	18,400	1.86
H5	EDA	1/12/2/0.323	1.30	16,900	1.13
H6	DETA	1/12/1/0.323	1.39	11,200	1.33
H7	DETA	1/12/2/0.323	1.31	9250	1.22

[a] The EDS of CPAAm was 3280%.

amine compounds. During the reaction, the isocyanate groups formed as transient intermediates, in the presence of excess alkali, react with water to yield the primary amine on the polymer chain, as shown in Eq. (1). It is also known that, the isocyanate groups react preferably with amine or alcohol rather than water, according to reactions (2) and (3) [4]. Thus, during the reaction carried out in the presence of amine, polymers with bisubstituted urea groups, along with primary amine groups, were obtained.

$$\text{–CONH}_2 + \text{NaOCl} \rightarrow \text{–CON}^-\text{Cl} \rightarrow (\text{–N=C=O}) \rightarrow \text{–NH}_2 \quad (1)$$

$$\text{–N=C=O} + \text{R–NH}_2 \rightarrow \text{–NHCONH–R} \quad (2)$$

$$\text{–N=C=O} + \text{R–OH} \rightarrow \text{–NHCOO–R} \quad (3)$$

The Hofmann reaction was carried out on CPAAm with different amounts of NaOCl, in the presence or absence of EDA and DETA. The reaction conditions and properties of products are given in Table 3. The products obtained from conventional Hofmann reactions in the absence of amine compounds were hard and sticky, but the others were white fine powders. The reaction carried out by using 0.3 mol NaOCl gave the product (H1) with the AV 1.26 mmol/g and an EDS 1900%. When the amount of NaOCl was increased to 1.0 (H2), the AV and EDS decreased probably due to side reactions [5]. The products obtained after the reactions carried out in the presence of amines had higher AV and higher EDS. The highest values were obtained from the reaction carried out by the use of 1.0 mol NaOCl along with EDA, which reacted with isocyanate group intermediate more easily than DETA (H4).

3.4. FT-IR spectra of polymers

The FT-IR spectra of CPAAm and the reaction products (TA9, TN2 and H4) with characteristic peaks [18,19] are given in Fig. 1. Additional peaks appear at about 1540 cm^{-1} (secondary amide groups and carboxylate groups) and 1395 cm^{-1} (carboxylate groups) [20] confirming a parallel hydrolysis reaction in transamidation reaction product in aqueous media(TA9). The peak at 1395 cm^{-1} was not present in the spectra of transamidation reaction product in nonaqueous media (TN2). The additional double peak at 1559–1545 cm^{-1} (H4) is attributed to the formation of bisubstituted urea groups [20] formed by the above mentioned reaction of the EDA with isocyanate intermediate.

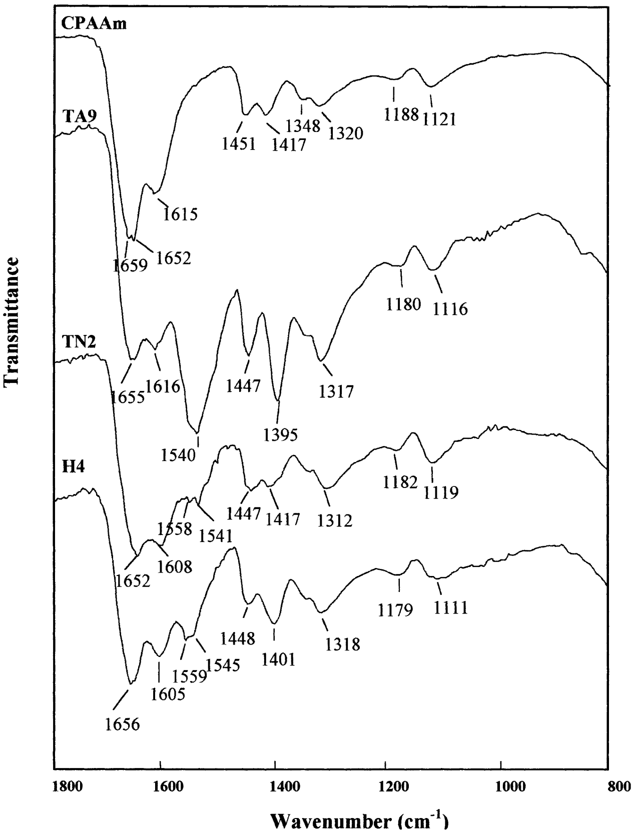

Fig. 1. The FT-IR spectra of CPAAm and modified reaction products (TA9, TN2 and H4).

3.5. Removal of copper (II) ion by modified polyacrylamides

The metal-ion complexation of polymeric ligands was found to be highly dependent on pH of medium [21,22]. This was confirmed by the increase in capacity of TA8 with increasing pH (Fig. 2). High adsorption at high pH values implies that Cu(II) ions interact preferably with unprotonated amine groups by chelating [23,24]. In this work, the Cu(II) ion removal capacities of the products were determined by batch equilibrium technique at moderate pH of 5.5, which was considered to be optimal to avoid the precipitation of cupric hydroxide [24].

As seen from Table 1, CPAAm is not effective in removal of Cu(II) ions since amide groups alone cannot form

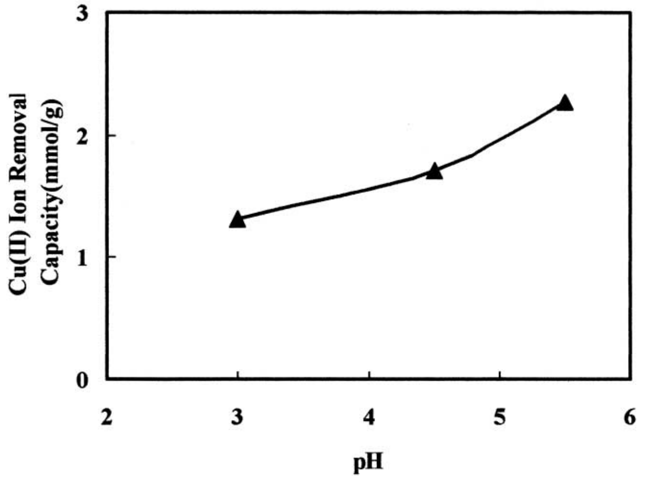

Fig. 2. The effect of pH on the Cu(II) ion removal capacity of TA8.

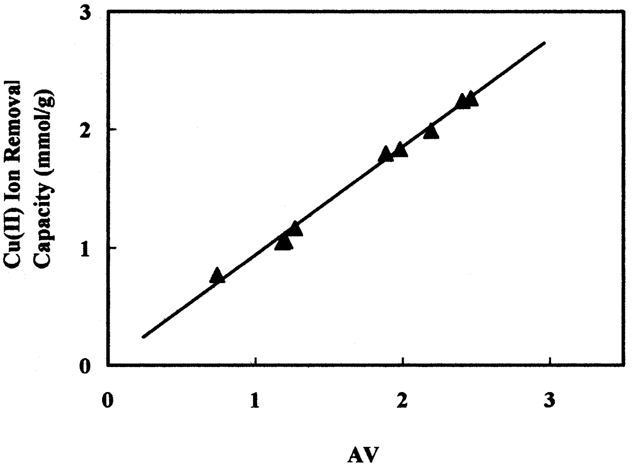

Fig. 3. The effect of AV on the Cu(II) ion removal capacity for the transamidation products (TA1–TA8).

complexes with copper ions [25]. Products of transamidation reactions in aqueous media (TA1–TA8) show a linear relationship of increase in AV, reaching a maximum of 2.27 mmol/g Cu(II) ion removal capacity for 2.46 mmol/g AV (Fig. 3, Table 1) This approximately 1/1 molar ratio amine chelating behavior was previously observed [11] although in our case carboxylate groups must have participated in chelating but also with a better utilization of total chelating groups than the guanidyl and carboxylate groups [26] and the glycine groups [27] of previous works. Nonaqueous transamidation products (TN1, TN2) had high AV but due to their low EDS, their Cu(II) ion removal capacities were also low (Table 2). It is quite probable that both groups of the amine reacted with the polymer, forming a layer of low permittivity.

Transamidation products in aqueous media (TA8) showed a stable removal capacity after regeneration with HCl (Table 4). However it is far more interesting that after a single regeneration cycle, the capacity of transamidation products obtained in nonaqueous media (TN1, TN2) increased significantly. Although, in literature, no previous mention of such behavior was found, a reasonable explanation would be the acid/alkaline cycle provided an ionization, which expanded the polymer matrix.

Products of Hofmann reaction in presence of amine (H3–H7) had much better EDS and somewhat higher AV than conventional Hofmann reaction products (H1, H2), which consequently provided better Cu(II) ion removal capacities (Table 3). Previously prepared similar amino functionalized polyacrylamides had maximal Cu(II) ion removal capacities of 1.67–2.41 mmol/g [10–12]. The transamidation products in aqueous media, nonaqueous media (regenerated) and modified Hofmann products prepared in this work had maximal ion removal capacities of 2.27, 2.93 and 1.86 mmol/g, respectively, and these compare well with previous transamidation products mentioned above. The selectivity of these modified polyacrylamides to different heavy metals shall be reported separately, in a future paper.

4. Conclusion

The transamidation and Hofmann reaction of CPAAm and LPAAm was more sensitive to increase of reaction temperature rather than the reaction time. Larger amine molecules decreased the swelling of the polymers due to increased crosslinking. Aqueous media reactions yielded products with additional carboxylate groups, due to competing hydrolysis reactions. Lack of hydrolysis in nonaqueous media reactions gave products with higher AV but lower EDS. AV and swelling degree of modified Hofmann reaction products with bisubstituted urea groups was better than conventional products. These polymers had promising

Table 4
The amounts of Cu(II) ions adsorbed/desorbed by some transamidation reaction products

Cycle[a]	TA8		TN1		TN2	
	Adsorbed Cu(II) ion (mmol/g)	Desorbed Cu(II) ion (mmol/g)	Adsorbed Cu(II) ion (mmol/g)	Desorbed Cu(II) ion (mmol/g)	Adsorbed Cu(II) ion (mmol/g)	Desorbed Cu(II) ion (mmol/g)
1	2.27	2.23	2.08	2.06	0.91	0.89
2	2.31	2.29	2.93	2.91	1.74	1.72
3	2.28	2.25	2.91	2.87	1.76	1.73

[a] See text for the cycle procedure.

properties as complexing agents for Cu(II) ion removal especially, in case of products with high AV and EDS. Also improvement in capacity due to expanding polymer matrix of nonaqueous media products after regeneration was found to be of interest.

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