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Water super absorbents based on copolymers of acrylamide with sodium acrylate

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Summary

Water absorbing materials on the basis of acrylamide copolymers have been investigated. The cross-linking of polymer chains strongly effects the degree of water absorption. The influence of starting composition of polyacrylamide : sodium hydroxide, duration of hydrolysis and irradiation conditions on cross-linking have been determined and optimized technological parameters have been derived. Water super absorbents with the ability to absorb up to 900g water by one gram material have been prepared.

Introduction

Recently, materials with the ability to absorb water in high amounts are again under investigation, because of their potential applications in communication technology, building industry, chromatography, water purification and agriculture (1-7). Especially polymers can absorb water up to few hundred times of their own weight (5,8). These polymers are often called water super absorbents or polymer hydrogels (9,10). Water super absorbents generally are low cross-linked hydrophilic electrolytes. Their high swelling degree has been mainly supported by following components: macromolecular polymer network and poly-electrolyte constituents (11) and investigated by different methods. (12,13). Omidian et. al (14) studied the swelling behavior and fitted it with mathematical relationships based on spring and dashpot models.

Water super absorbents are often based on water-soluble polymers, in particular, on statistic copolymers of acrylamide (AA) with acrylic acid and its salts, cross-linked by chemical or radiation techniques (6, 9, 15-21). A radiation technique is more preferable than a chemical one, because of the advantage to control gently the level of cross-linking by variation of the absorbed dose.

Copolymers of AA with acrylic acid and its salts can be obtained by copolymerization of the monomers e.g. used in a manufacturing process of polyacrylamide (PAA) (22,23). It is known that an optimal content of the ionized carboxyl groups in copolymer, which provide maximal water absorption, should not exceed 30 Mol % (20,24). The composition of the commercial available PAA depends substantially on the production conditions. To increase the content of carboxyl groups an alkaline hydrolysis of PAA is carried out. The possibility to produce water super absorbents based on alkaline hydrolysis

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products has been previously shown (25,26). However, there are still no data about the dependence of water absorption value on PAA hydrolysis conditions and post-hydrolysis radiation cross-linking.

This paper deals with the influence of the content of acrylamide copolymer and sodium acrylate and the conditions of radiation cross-linking on the degree of water absorption by the water super absorbent material.

Experimental

Granulated PAA, obtained by the sulphate method (AA is obtained from acrylonitrile over sulphuric acid (22)), was used as an initial polymer with a content of carboxyl groups not higher than 3 Mol %. For alkaline hydrolysis a 5% water solution of the polymer prepared by PAA dissolution with distilled water at 70°C has been used. Hydrolysis was carried out at 70°C during 3 hours at a mole ratio of PAA:NaOH equal to (A) 1.0:0.1, (B) 1.0:0.33 or (C) 1.0:1.0, respectively. During the hydrolysis after 5, 20, 60 and 180 min samples of the solution were taken followed by 2-4 times precipitation in acetone to washing out the polymer from alkaline excess. The samples were dried and dissolved with distilled water.

Carboxyl group content was determined by reverse titration method (27) and IR spectroscopy (28). The molecular mass distribution of the initial non-cross-linked PAA has been determined by a commercial Ophenomenex® system, combined with 2 columns (Hema Bio 100, Hema Bio Linear). The columns were calibrated with styrene samples. A 0.05 molar solution of $NaNO_3$ was used as an eluent at 1 ml/min eluation rate. The detection system consisted of a refraction detector (RI-930, Jasco) and a laser light scattering detector (Dawn DSP, Wyatt) working at a wavelength of 632.8 nm. The solutions sampled during the duration of hydrolysis were irradiated at room temperature with a γ-source Cs^{137}, dose power equal 0.35 Gy/s. After the irradiation the polymeric material has been precipitated in acetone and dried at 90-100°C. The water absorption degree α was calculated from experimental data by following equation

$$\alpha = (m_2 - m_1) / m_1 \qquad /1/$$

where m_1 is the initial mass of the investigated dry sample, m_2 is the mass after 48 hour of swelling in distilled water at a room temperature.

For the determination of the molecular mass distribution of the prepared copolymers obtained by alkaline hydrolysis the alkaline excess has to be neutralized with 99% acetic acid to a final pH value of the hydrolysate from 6,5 to 7,0 and with a hydrolysate density of 1,052 g/cm^3.

Results and Discussion

The results of the determination of the molecular mass distribution of the initial PAA and of the hydrolized one by molar ratio PAA : NaOH = 1.0 : 1.0 are shown in the table 1. For the initial industrial PAA (Table 1, Sample 1) the average values of the molecular weight moments M_n (average molecular weight), M_w (weighted molecular weight) and M_z (centrifuge molecular weight) are close to $(2.1 - 2.9)\cdot 10^6$ g/mol. The ratios M_w / M_n and M_z / M_n , which characterize polydispersity, are close to 1 that indicate comparatively narrow molar mass distribution of this sample. For the hydrolized industrial PAA (Table 1, Sample 2) the average values M_n, M_w, and M_z are 1.3 - 1.6 times smaller then the corresponding values M_n, M_w, and M_z for the initial industrial PAA. Hence, the alkaline hydrolysis of the industrial PAA in water solution of natrium hydroxide is not practically accompanied by the hydrolytic destruction of the main chain of the macromolecules of the copolymer.

Sample No	Content of the functional groups in the copolymer, mass %		M_n, 10^{-6}	M_w, 10^{-6}	M_z, 10^{-6}	M_w/M_n	M_z/M_n
	Amide	Carboxyl	g/mol				
1	97	3	2.087±0.06	2.374±0.08	2.934±0.06	1.138±0.052	1.406±0.145
2	25	75	1.605±0.30	1.687±0.40	1.796±0.90	1.051±0.313	1.119±0.588

Table 1. Characteristics of the macromolecules structure of the AA copolymers using the molecular weight moments M_n (average molecular weight), M_w (weighted molecular weight) and M_z (centrifuge molecular weight), all in g/mol.

During PAA hydrolysis the amide groups transform into carboxyl groups. This is confirmed by the data of the IR spectra (Fig. 1). There is an absorption band at 1650 cm^{-1} in the IR spectra of the hydrolysis product that corresponds to the amide groups. The band at 1550 cm^{-1} is attributed to the carboxyl groups. On the other hand there is no band at 1720 cm^{-1} that could been assigned to the absorption band of the unionized carboxyl groups. Hence, the carboxyl groups are almost completely ionized.

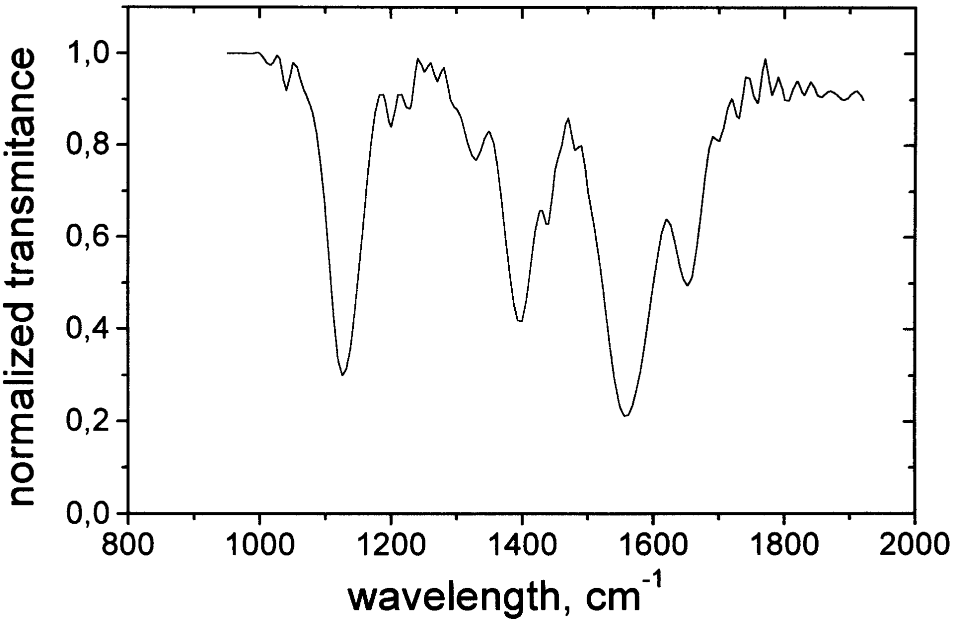

Figure 1. IR spectra of hydrolyzation products.

Figure 2 shows the transformation degree dependent on hydrolysis time. Obviously, the curves tend to reach a limit. About 5 minutes after the hydrolysis start the reaction reaches a transformation degree of 65-70% of the limiting value at a time of 180 min. The transformation degree increases monotonously with a decrease of PAA:NaOH ratio. It should be noted that the practically determined limiting values consist only of 50-80% of theoretically possible value at the given alkaline quantity. This seems to be caused by the fact that carboxyl groups, which are created during hydrolysis, prevent the interplay of hydroxyl groups of the alkaline with amide groups of the copolymer.

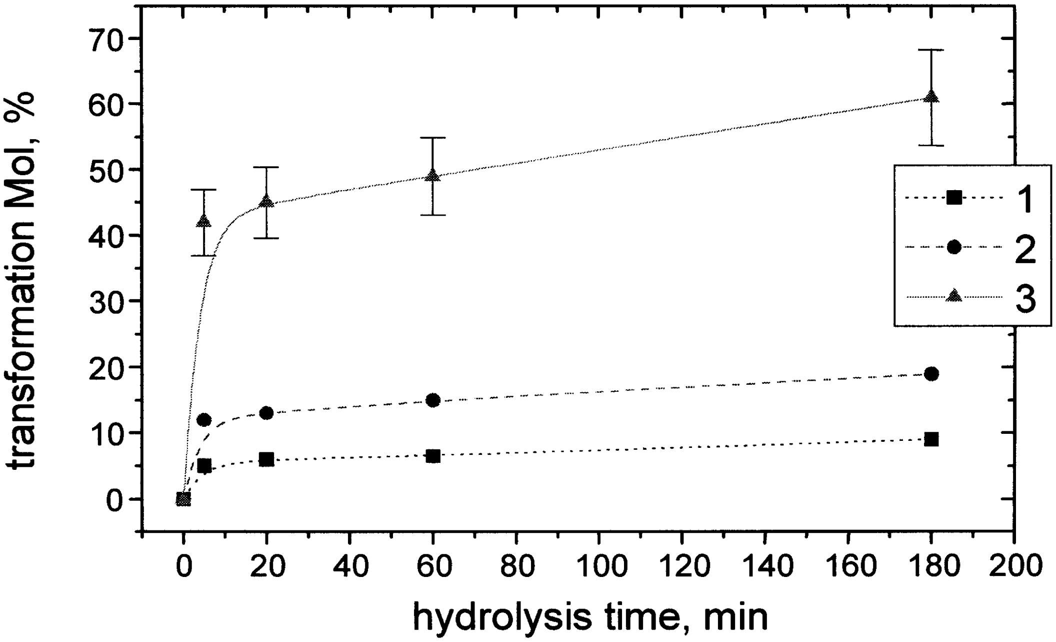

Figure 2. Dependence of amide groups transformation into carboxyl groups on hydrolysis time. Sample 1, 2 and 3 with molar ratio of PAA:NaOH 1.0:0.1, 1.0:0.33 or 1.0:1.0, respectively.

The hydrolysates obtained at PAA:NaOH ratio = 1.0:1.0 were not significantly cross-linked at doses up to 50 kGy At PAA:NaOH ratio = 1.0:0.33 and 1.0:0.1 a cross-linking starts already at doses of 2-3 kGy. The ability to absorb water (α value) decreases with increased irradiation dose. Figure 3 gives an overview about the influence of irradiation dose on the α value of materials with different molar ratio PAA:NaOH and different hydrolysis time. The α value of the hydrogel at a given irradiation dose is mainly determined by the ratio of PAA:NaOH and only slightly by the a hydrolysis time. The maximum value for α (900 g of water per 1 g of hydrogel copolymer) was achieved at the ratio PAA:NaOH = 1,0:0,33 and at an exposition dose of 5 kGy. The transformation degree of the amide groups into carboxyl groups reaches in this material a saturation level of about 12% (see Fig.2). It should be pointed out that the application of high irradiation dose (50 kGy) forces a strong cross-linking in all investigated materials. It seems that this belongs to the polydispersity of the initial PAA and, as a consequence, also to the products of alkaline hydrolysis.

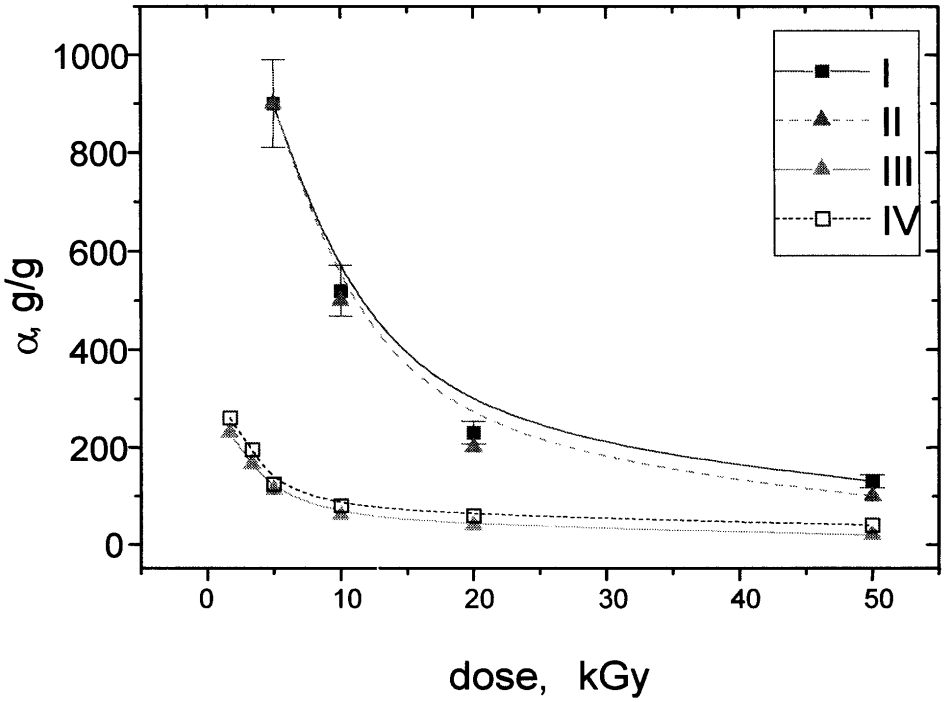

Figure 3. Dependence of water absorption degree α of water absorbent materials on irradiation dose. Samples I, II with molar ratio PAA:NaOH 1.0:0.33, sample III, IV 1.0:0.1. The time of hydrolysis was 5 min (sample I, III) or 60 min (II, IV), respectively.

In conclusion we found that by means of alkaline hydrolysis of commercial PAA with low initial content of carboxyl groups hydrogels can be obtained. The employment of ionizing radiation to achieve cross-linking is an important step to produce materials with high ability to absorb water. Using the described preparation conditions we achieved transformation degree of the amide groups into carboxyl groups in the range of 12%. The dose applied for preparation of water super absorbents with a high swelling degree has to be as low as possible, but high enough for the cross-linking of the hydrolysated PAA. In the case of PAA with transformation degree of the amide groups into carboxyl groups equal to 12-13% such a dose is 3-5 kGy. One gram of the prepared water super absorbent material can absorb up to 900g water at room temperature. It should be noted that similar results were obtained using acrylonitrile copolymers as starting material.

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