Functional Polymers Based on Acrylamide Crosslinked Copolymers

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Summary: Crosslinked copolymers of acrylamide were obtained by the aqueous suspension polymerization method. Divinylbenzene and N,N'-methylene-bis-acrylamide were used as crosslinking agents. Ethylacrylate was used as a third comonomer. The real acrylamide content in the crosslinked copolymers was calculated taking into account the found nitrogen content after the removal of the soluble fractions. The water uptake in dependence on the copolymer structure gave information on the hydrophilicity of these copolymers. Hofmann degradation of the amide groups led to copolymers containing vinylamine functional groups, which were characterized by IR spectroscopy and by anion exchange capacity. Carboxylic groups were generated by the alkaline hydrolysis of the ester groups.

Introduction

The presence of primary amine groups in the soluble and crosslinked copolymers is of a great interest due to their high reactivity which allows the incorporation of other additional moieties.[1-5] Producing of monofunctional weakly basic anion exchangers with primary amine groups is a difficult task. The reaction of chloromethylated styrene-divinylbenzene copolymers with ammonia gives usually a polyfunctional anion exchanger. A less explored way to get weak basic anion exchangers with primary amine groups is Hofmann degradation of the amide groups contained in a crosslinked copolymer of acrylamide. Crosslinked copolymers of acrylamide by their high hydrophilicity are very suitable tools for the separation of biopolymers. A great interest is now remarked to obtain macroporous copolymers of acrylamide with N,N'-methylene-bis-acrylamide as a crosslinking agent.[6] The aim of our paper is to obtain crosslinked copolymers of acrylamide with divinylbenzene and N,N'-methylene-bis-acrylamide as crosslinking agents by the suspension polymerization technique in aqueous medium, on

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one hand, and to transform the amide groups in primary amine groups by Hofmann degradation, on the other hand. In order to obtain copolymers as beads and to diminish drastically the fraction of the acrylamide which usually is found as a water soluble homopolymer we used the following conditions: a high salt content in the aqueous phase, an aliphatic alcohol with a low solubility in water to solve the acrylamide and a third comonomer with a low solubility in water have been used. The third comonomer preffered in our experiments was the ethylacrylate because some amphoteric ion exchangers could be prepared by the subsequent hydrolysis of the ester groups after the Hofmann degradation of the amide groups. The influence of the crosslinking agent nature on the properties of both the crosslinked copolymers and of the ion exchangers was followed.

Experimental

Materials

Acrylamide (AA) purchased from Fluka was recrystalized from methanol. Ethylacrylate, technical grade, was fresh distilled at 760 mmHg. Divinylbenzene (DVB) purchased from Dow Chemical, also technical grade, was distilled at 3 mmHg before use (62.5 % o-, m-, p-DVB, 50.05 % ethylstyrene, 7.45 % inert compounds). 2-Ethyl-1-hexanol (2EH) was distilled at 183.5° C and 760 mmHg. Benzoyl peroxide (POB) was employed as polymerization initiator.

Copolymer synthesis and chemical transformations

Crosslinked copolymers of acrylamide as beads were obtained by aqueous suspension polymerization technique. Acrylamide and N,N'-methylene-bis-acrylamide (when it was used as crosslinking agent) were first disolved in 2EH and then mixed with the other comonomers. POB (1-1.2 wt.-%) was disolved in ethylacrylate. The polymerization temperature was mentained at 78-80° C for 12 hours; afterwards, the suspension was cooled down and the copolymer beads were sieved and washed with warm water and the bead fraction 0.125-1.00 mm was collected. Removal of the 2EH was performed by methanol extraction. The water soluble homopolymer was removed with boilling water.

The yield in the dry beads was around 95 %.

Hofmann degradation of amide groups was performed mainly in the following conditions: on about 15 mL wet copolymer (previously equilibrated with water for 48 h), cooled at 0°C, a volume of NaOCl with 14 wt.-% chlorine and 10 wt.-% NaOH cooled at about –5° C, enough to cover the beads, was added under the stirring. The whole reaction mixture was cooled at about –18° C for 4 h and then the temperature was allowed to increase to 18° C for 5h.

The hydrolysis of the ester groups was performed with NaOH 10 wt.% at 98° C, for 10 h, either on the copolymers with nontransformed amide groups or on the copolymers with primary amine groups (after the Hofmann degradation).

Characterization methods

The dry beads were first characterized by the nitrogen content in order to establish the real content of AA. The chemical transformation of amide groups in primary amine groups and the hydrolysis of the ester groups to carboxylic groups was followed by IR spectroscopy. The IR spectra were recorded with a Perkin-Elmer 577 IR spectrophotometer in the range of 4000-400 cm^{-1}.

The specific density (ρ_{sp}) was measured in n-heptane. The apparent density (ρ_{ap}) was determined using a mercury picnometer at 13 mPa. The water uptake (Q_w) was determined by centrifuging the copolymers and ion exchangers at 500 G following an immersion for 48 h in water. The ion exchange capacity was measured according to the functional group nature of the transformed copolymers. First, the ion exchangers were conditioned by alternate passing of 4 wt. % NaOH and 4 wt. % HCl aqueous solutions. The anion exchange capacity of the copolymers containing primary amine groups (after the Hofmann degradation) was determined as before.[7] The cation exchange capacity (after the hydrolysis of the ester groups) was determined by H_3O^+/Na^+ ion exchange. About 15 mL wet ion exchanger was put into a glass column fitted with a sintered glass disk at the bottom. An aqueous solution of 4 wt.-% HCl was passed through the column followed by washing with distilled water until a neutral pH value was reached. With this procedure the carboxylate groups were thus transformed to carboxylic groups. A measured amount of 1 M HCl (V_l) was passed through the column and the eluent was titrated with 1 M NaOH (V_2). The cation exchanger sample was quantitatively removed from the column in a graded cylinder and its volume was measured (V_a). The volumetric exchange capacity was calculated as follows:

Weak acidic exchange capacity (meq/mL) = $(V_l - V_2)/V_a$

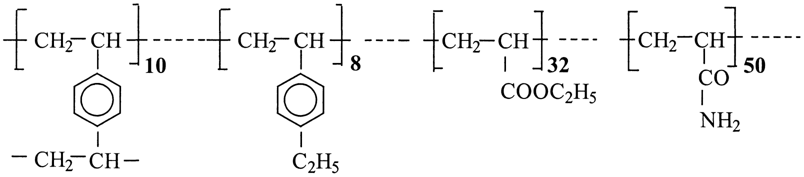
The wet cation exchange sample was dried and then weighted (m, g). The massic cation exchange capacity was then calculated:

Weak acidic exchange capacity (meq/g) = $(V_l - V_2)/m$

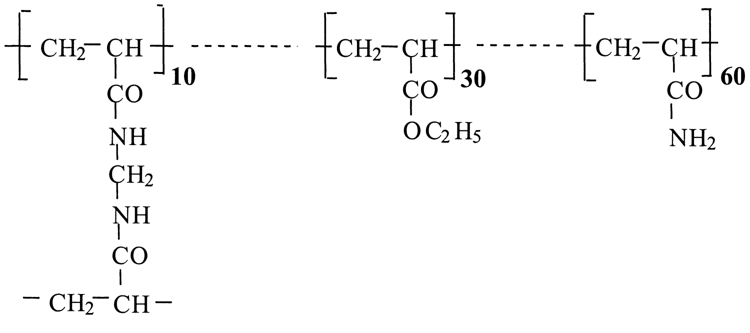
Results and discussion

AA crosslinked copolymers - synthesis and characterization

The chemical structures of two different copolymers which were synthesized in this work are presented in Scheme 1. Comonomer contents mean weight % calculated for the starting organic phase.



Copolymer AA3



Copolymer AA8

Scheme 1.

Table 1. Composition of some AA crosslinked copolymers.

Sample	Crosslinking agent		Ethyl acrylate	Acrylamide content, wt.-%	
		wt.-%	wt.-%	Calc.	Found
AA3/9[a)]	DVB	10	32	50	45
AA3/13[b)]	DVB	10	32	50	46.5
AA3/17[c)]	DVB	10	32	50	47
AA8	MBAA	10	30	60	58
AA9/1	MBAA	8	30	62	60

[a)] 3 wt.-% of NaCl in the aqueous phase; [b)] 4 wt.-% of NaCl in the aqueous phase; [c)] 5 wt.-% of NaCl in the aqueous phase.

Crosslinked copolymers of AA as beads are usually obtained by the inverse suspension polymerization due to the high solubility of AA in water.[8] We succeeded to perform aqueous suspension polymerization of AA reducing the solubility of AA by three parameters: a high content of NaCl up to 4-6 wt.-% in the aqueous phase, an aliphatic alcohol (2EH) was used in the organic phase in order to solve AA and a less hydrophilic comonomer was also used (ethylacrylate). In this way the yield in crosslinked copolymer increased up to 95 %. The composition of some crosslinked copolymers of AA in dependence on the crosslinking agent nature and content is shown in Table 1. The found content of AA was also included. Three different samples of copolymers with 10 wt. % DVB prepared in the presence of 3, 4 and 5 wt.-% of NaCl in the aqueous phase, respectively, were presented in Table 1 which show the increase of the AA content with the increase of the NaCl concentrantion.

The AA crosslinked copolymers in the dry state were characterized also from the morphological point of view, the values of Q_w, ρ_{sp}, and ρ_{ap} are collected in Table 2. As can be seen from Table 2, the Q_w values of the copolymers with MBAA as crosslinking agent are much higher than those obtained with DVB. A higher hydrophilicity is specific for such copolymers. Some porosity of these copolymers can be also remarked which values are significant mainly in the case of poly (AA-co-EA-co-MBAA) since 2EH was present in the organic phase. Aliphatic alcohols with 6-8 carbon atoms have been successfully used as porogens to obtain porous poly (AA-co-MBAA) monolithic rods.[1)]

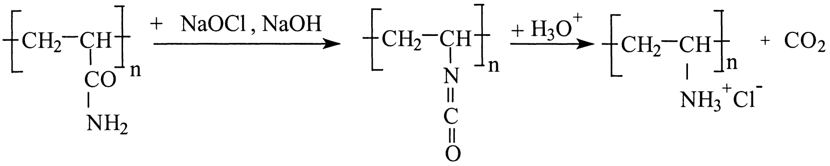
Table 2. Morphological characteristics of the acrylamide crosslinked copolymers.

Sample	Q_w g/g	ρ_{sp} g/mL	ρ_{ap} g/mL	$P^{a)}$ %
AA3/9	0.68	1.177	1.051	10.7
AA3/13	0.75	1.162	1.137	2.15
AA3/17	0.67	1.169	1.121	4.10
AA8	1.57	1.186	1.028	13.32
AA9/1	1.55	1.160	1.030	11.20

a) Porosity was calculated according to: $P = (1- \rho_{ap}/\rho_{sp}) \times 100$

Hofmann degradation of amide groups contained in AA-crosslinked copolymers

Hofmann degradation of amide groups contained in homo- and linear copolymers of AA has been already reported.[1-3] The mechanism of this reaction is well known and only the global reaction is presented in Scheme 2.



$$[CH_2-CH(CONH_2)]_n \xrightarrow{+\ NaOCl,\ NaOH} [CH_2-CH(N{=}C{=}O)]_n \xrightarrow{+\ H_3O^+} [CH_2-CH(NH_3^+Cl^-)]_n + CO_2$$

Scheme 2.

As a secondary reaction the hydrolysis of amide groups to carboxylic groups has been remarked.[1,3] The first qualitative evaluation of the Hofmann degradation reaction in our study were the IR - spectral changes comparative with the starting copolymers. The characteristic absorption bands of the poly(AA-co-AE-co-DVB) and poly(AA-co-AE-co-MBAA) were the followings: a specific band for the ethyl groups contained in AE and ethylstyrene at 2900-3000 cm^{-1}, the band at 1740 cm^{-1} was assigned to the C=O stretch from the ester groups, a strong band at 1665 cm^{-1} assigned to the stretching vibrations of the C=O bond from amide groups, a band near 1170 cm^{-1}, which was found in the IR spectra both, before and after the Hofmann degradation, assigned to the C—N stretch, and the intensity of all these absorption bands was depending on each copolymer composition. After the Hofmann degradation, the bands at 2900-3000, 1740, and 1170 cm^{-1} increased in their intensity; the bond of the C=O bond of the amide groups diminished. The characteristic band of the COO^- groups, near 1570 cm^{-1}, which must be present if the hydrolysis of the ester groups is significant as a secondary reaction, was not evidenced. A large band between 1550-1600 cm^{-1} was found only when the hydrolysis of the ester groups was performed at 98° C with an aqueous solution of 10 wt.-% NaOH. This is an evidence that the Hofmann degradation of the amide groups in the conditions used in this study was not accompanied by the formation of the COO^- groups in a detectable amount.

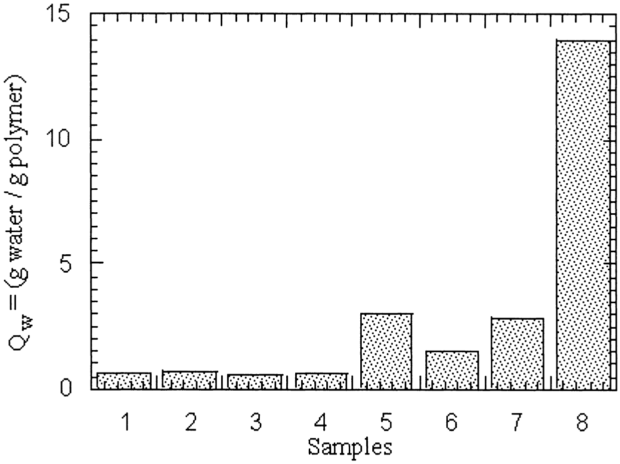


Figure 1. Samples according to Table 1:1= AA3/9; 2 = AA3/9 after Hofmann degradation; 3 = AA3/17; 4 = AA3/17 after Hofmann degradation; 5 = AA3/17 after hydrolysis; 6 = AA8; 7 = AA8 after Hofmann degradation; 8 = AA8 after hydrolysis.

Information on the properties of the starting and transformed copolymers were also obtained by comparison the water uptake (Q_w) values which were included in Figure 1. As can be seen, the Q_w values of the poly(AA-co-AE-co-DVB) after the Hofmann degradation are similar with those before the transformation. The presence of the COO^- groups after the hydrolysis of the ester groups led to a significant increase of the Q_w values. The Q_w values after the hydrolysis of the ester groups contained in the poly(AA-co-AE-co-MBAA) increased about seven times compared to the starting copolymer.

Some ion exchange capacities values were collected in Table 3. Weak basic anion exchangers with primary amine groups and weak acidic cation exchangers with significant ion exchange properties were obtained. The influence of the crosslinking agent's nature on the ion exchanger properties is reflected in the lower values of the ion exchange capacities per volume when the crosslinking agent was MBAA comparative with DVB. The massic ion exchange capacities are in a reverse order.

Table 3. Ion exchange capacities of the transformed copolymers.

Sample[*)]	$\frac{C_S}{meq/mL}$		$\frac{C_S}{meq/g}$	
	Weak basic	Weak acidic	Weak basic	Weak acidic
AA3/9 H	1.3	-	5.52	-
AA3/17 H	0.68	-	3.10	-
AA3/17 h	-	1.53	-	5.19
AA3/17 H+h	0.89	1.18	2.64	3.26
AA8 H	0.18	-	5.62	-
AA9 H	0.31	-	8.21	-

[*)] H - Polymer with primary amine groups obtained by Hofmann degradation;
h - Polymer with carboxylic groups obtained by hydrolysis.

Conclusions

Crosslinked copolymers with a high content of AA were obtained by suspension polymerization technique with both, DVB and MBAA as crosslinking agents. The AA content, after the polymerization and removal of the soluble components, was determined by nitrogen analysis. Hofmann degradation of amide groups led to the functional polymers with primary amine groups. The amide group transformation was evidenced by IR spectroscopy and weak basic exchange capacity. Alkaline hydrolysis of the ester groups led to carboxylic groups which were evidenced by IR spectroscopy and weak acidic exchange capacity.

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