Ion-Exchange Resins. II. Acrylamide Crosslinked Copolymers as Precursors for Some Ion Exchangers

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ABSTRACT: Crosslinked copolymers of acrylamide (AA) and ethylacrylate and some ion exchangers derived from them containing either primary amine groups, obtained by the Hofmann degradation of the amide groups, or carboxylic groups, obtained by the alkaline hydrolysis of the ester groups, were studied. Divinylbenzene and *N,N'*-methylenebisacrylamide were used as crosslinkers. The starting copolymers and the corresponding ion exchangers were characterized by IR spectroscopy, swelling behavior, and thermogravimetric analysis. The ion-exchanger properties were correlated with the crosslinker nature and the chemical reactions performed on the AA copolymers. The average molecular weight between two crosslinks, determined from the swelling data in water, was compared with that calculated on the basis of the copolymerization stoichiometry only for the carboxylic cation exchangers. In this way, the preservation of the crosslink density after the hydrolysis was revealed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2701–2707, 2003

Key words: crosslinking; degradation; ion exchangers; infrared spectroscopy; thermogravimetric analysis (TGA)

INTRODUCTION

Synthetic ion exchangers, in bead form, are the most frequently used materials for solving the concentration and separation problems of inorganic and organic ions in both industry and academia. The most commonly used starting copolymers for obtaining ion exchangers with different functionalities and morphologies are still styrene–divinylbenzene (S–DVB) copolymers.[1–4] Among functional polymers, linear and crosslinked copolymers bearing primary amine groups are of a great interest because of their high reactivity, which allows the incorporation of numerous additional moieties.[5–9] However, ion exchangers with primary amine groups are difficult to obtain by chemical reactions of S–DVB copolymers. A less explored way of obtaining anion exchangers with primary amine groups is Hofmann degradation of the amide groups contained in a crosslinked copolymer of acrylamide (AA). For this purpose, we synthesized AA copolymers as beads by the suspension polymerization technique. This technique is usually less employed because of the high solubility of AA in water. To reduce drastically the fraction of AA in the aqueous phase, we used the following conditions: a high content of NaCl in the aqueous phase, an aliphatic alcohol with low solubility in water as a solvent for AA [2-ethyl-1-hexanol (2EH)], and a third comonomer with

low solubility in water.[10] Ethylacrylate (EA) was employed as the third comonomer because some carboxylic cation exchangers could easily be prepared by the hydrolysis of the ester groups. Some amphoteric ion exchangers could also be obtained by the subsequent hydrolysis of the ester groups after the Hofmann degradation of the amide groups. Therefore, the molecular structures of both the starting copolymers and the derived ion exchangers were quite complicated. The aim of this study was to correlate the synthesis conditions of the AA copolymers with the properties of the ion exchangers derived from them. IR spectroscopy, swelling behavior, and thermogravimetric analysis (TGA) were used to obtain further information on the AA crosslinked copolymer structure and on the structural changes taking place on account of the chemical reactions of these copolymers. Swelling data in water gave some information on the crosslink density before and after the chemical reactions of the crosslinked copolymers.

EXPERIMENTAL

Materials

AA, purchased from Fluka (Buchs, Switzerland), was recrystallized from methanol. *N,N'*-Methylenebisacrylamide (MBAA), purchased from Merck (Rahway, NJ), was used as received. 2EH, used as a solvent for AA and MBAA, was distilled at 183.5°C and 760 mmHg. Technical-grade EA was freshly distilled at 760 mmHg. Divinylbenzene (DVB), purchased from Dow Chemical (Midland, MI) and also technical-

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TABLE I
Some Characteristics of the AA Crosslinked Copolymers

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Copolymer	Crosslinker			EA		AA		
						wt %		mol %
	Type	wt %	mol %	wt %	mol %	Calcd.	Found[a]	Calcd.
$(AA_{50}–EA_{32}–ES_8–DVB_{10})_1$[b]	DVB	10	6.63	32	27.55	50	45	60.6
$(AA_{50}–EA_{32}–ES_8–DVB_{10})_2$[c]	DVB	10	6.63	32	27.55	50	47	60.6
$(AA_{60}–EA_{30}–MBAA_{10})$	MBAA	10	5.36	30	24.79	60	58	69.83
$(AA_{62}–EA_{30}–MBAA_8)$	MBAA	8	4.24	30	24.49	62	60	71.27

[a] Determined on the basis of the nitrogen content of the copolymers after the homopolymer removal.
[b] BPO (1.3 wt %) in the copolymer synthesis; the weight difference in the theoretical copolymer structure was caused by the ES contained in the technical DVB; for 10 wt % DVB, the ES contribution was 8 wt %.
[c] BPO (1.5 wt %) in the copolymer synthesis; the weight difference in the theoretical copolymer structure was caused by the ES contained in the technical DVB; for 10 wt % DVB, the ES contribution was 8 wt %.

grade, was distilled at 3 mmHg before use (62.5% o-DVB, m-DVB, and p-DVB; 50.05% ethylstyrene (ES); and 7.45% inert compounds). Benzoyl peroxide (BPO) was employed as a polymerization initiator after two recrystallizations from methanol.

Methods

Crosslinked copolymers of AA as beads were obtained by an aqueous suspension polymerization technique according to a method previously reported.[10] The copolymer beads were sieved and washed with warm water, and a bead fraction of 0.125–1.00 mm was collected. The removal of 2EH was performed by methanol extraction. The AA homopolymer, which could be formed at the same time with the crosslinked copolymer, was completely removed with water in a Soxhlet extractor. Some characteristics of the AA copolymers studied in this article are summarized in Table I. The numbers in the copolymer name indicate the weight percentages of every monomer present in the monomer mixture.

In the synthesis of the crosslinked copolymers containing vinyl amine units, we followed mainly the method proposed by Tanaka and Senju[5] for the Hofmann degradation of amide groups from polyacrylamide. The differences in the experimental conditions used in this work were mainly due to the specific conditions required for the chemical reaction of crosslinked copolymers. Therefore, a volume of NaOCl (14 wt % chlorine and 10 wt % NaOH), cooled at about −5°C, that was sufficient to cover the beads was added under stirring to about 15 mL of wet copolymer (previously equilibrated with water for 48 h) cooled at 0°C. 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 5 h. The weak basic anion exchanger so obtained was then filtered and washed intensively with distilled water until a neutral pH was obtained. The hydrolysis of the ester groups was performed with 10 wt % NaOH at 98°C for
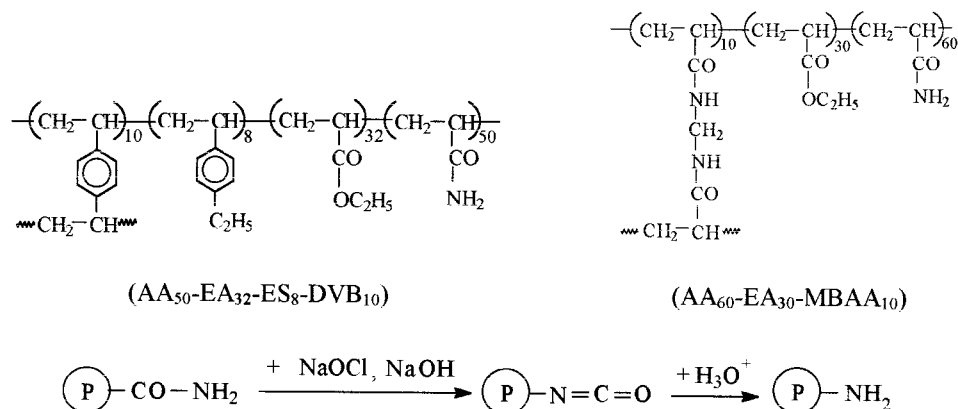
10 h. The cation exchanger, in bead form, was filtered and washed intensively with distilled water until a neutral pH was obtained. All samples were vacuum-dried at 50°C for 48 h before characterization in the dry state. The ion exchangers were also characterized by their weak basic ion-exchange capacity[11] (those containing primary amine groups) and by their weak acidic ion-exchange capacity[10] (hydrolyzed copolymers).

The IR spectra were recorded with a SPECORD M80 (Carl Zeiss, Jena, Germany) spectrophotometer in the range of 4000–400 cm^{-1} with the KBr pellet technique. The specific density was measured in n-heptane. The apparent density was determined with a mercury pycnometer at 13 mPa.[12] The swelling of the starting and transformed copolymers in equilibrium with a pure solvent was performed in water according to a technique previously described.[13] TGA was performed with a 50-mg powder sample at a heating rate of 9°C/min up to 900°C in air with a Paulik–Paulik–Erdey derivatograph (Budapest, Hungary); α-Al$_2$O$_3$ was used as the reference material.

RESULTS AND DISCUSSION

Synthesis of the ion exchangers

The theoretical structures of the starting copolymers of AA, according to the composition of the monomer mixture, and the global reaction of the Hofmann degradation of the amide groups are presented in Scheme 1. The hydrolysis of the amide groups into carboxylic groups, as a secondary reaction, was previously reported for the Hofmann degradation of polyacrylamide[5] and some linear copolymers of AA.[7] The influence of the starting copolymer structure on this secondary reaction was also followed in this study. Beads of $(AA_{50}–EA_{32}–ES_8–DVB_{10})_1$, before and after the Hofmann degradation, can be seen in Figure 1. The Hofmann degradation conditions preserved the spherical shape of the anion exchanger.

$$-(CH_2-CH)_{10}(CH_2-CH)_8(CH_2-CH)_{32}(CH_2-CH)_{50}$$

with pendant groups:

C_2H_5 / CO–OC_2H_5 / CO–NH_2

$\sim\sim CH_2-CH\sim\sim$

(AA$_{50}$-EA$_{32}$-ES$_8$-DVB$_{10}$)

$$-(CH_2-CH)_{10}(CH_2-CH)_{30}(CH_2-CH)_{60}$$

CO / NH / CH_2 / NH / CO

CO–OC_2H_5

CO–NH_2

$\sim\sim CH_2-CH\sim\sim$

(AA$_{60}$-EA$_{30}$-MBAA$_{10}$)

$$\bigcirc\!\!P\,-CO-NH_2 \xrightarrow{+\ NaOCl,\ NaOH} \bigcirc\!\!P\,-N=C=O \xrightarrow{+H_3O^+} \bigcirc\!\!P\,-NH_2$$

Scheme 1

The values of the ion-exchange capacity and water uptake (Q_w) of the ion exchangers studied in this work are included in Table II. The theoretical ion-exchange capacities (C_{gt}) were calculated with the following relationship:

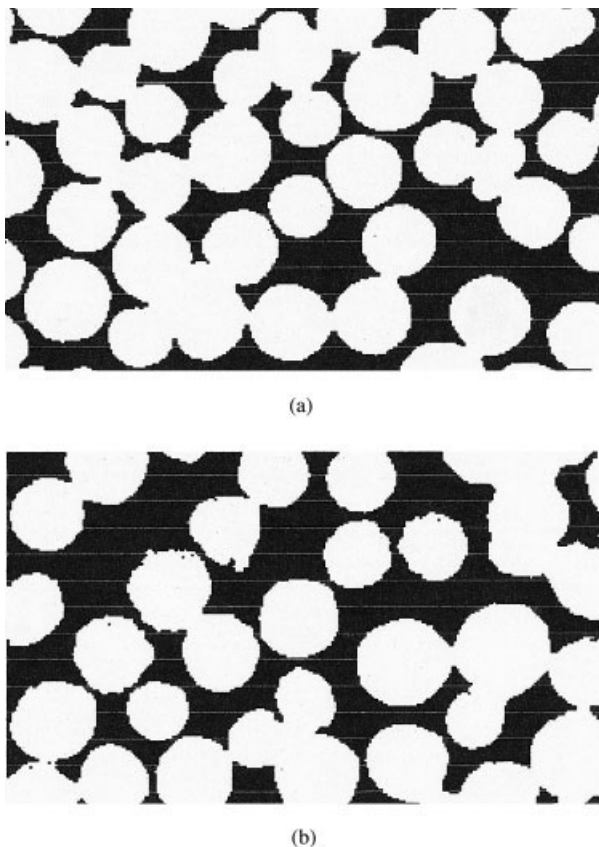$$C_{gt} = 10^3 \times a/[(100 - a) \times M_{ui} + a \times M_{ut}] \quad (1)$$

(a)

(b)

Figure 1 Beads of the (AA$_{50}$–EA$_{32}$–ES$_8$–DVB$_{10}$)$_2$ copolymer (a) before and (b) after the Hofmann degradation (original magnification = 15×).

where a is the weight percentage of the monofunctional monomer (AA or EA), M_{ui} is the molar mass of the initial monofunctional monomer (AA or EA), and M_{ut} is the molar mass of the transformed monomer unit (vinyl amine or sodium acrylate).

As can be seen in Table II, the weak basic anion-exchange capacity found after the Hofmann degradation was lower than that expected if all amide groups had been transformed into primary amine groups. This shows that not all the amide groups were involved in this process; some of them could still be present in the copolymer after the Hofmann degradation. That is, the real structure of the copolymer after the Hofmann degradation contained AA units in addition to the vinyl amine units. Another aspect evident in Table II was the higher value of the weak acidic cation-exchange capacity found after the alkaline hydrolysis of the ester groups in comparison with the calculated values. The difference shows that some of the amide groups were also transformed into carboxylate groups. The real amount of AA that was transformed into vinyl amine units and the fraction of AA that was transformed into sodium acrylate units could be calculated with the found values of the ion-exchange capacity. For example, with the found value of the anion-exchange capacity for (AA$_{50}$–EA$_{32}$–ES$_8$–DVB$_{10}$)$_1$H, which, according to Table II, was 5.21 mequiv/g, the real amount of transformed AA was calculated with eq. (1), this being around 32.3 wt % instead of 45 wt %, which was the content of AA in the starting copolymer. We can also observe the values of Q_w, which were relatively low after the Hofmann degradation and very high after the hydrolysis of the ester groups.

IR spectroscopy

The IR spectra of the (AA$_{50}$–EA$_{32}$–ES$_8$–DVB$_{10}$)$_1$ copolymer and the derived ion exchangers are shown in

TABLE II
Some Characteristics of the Ion Exchangers Synthesized from AA-Crosslinked Copolymers

Sample[a]	Weak basic ion-exchange capacity (meq/g)		Weak acidic ion-exchange capacity (meq/g)		$Qw/(g/g)$
	Calcd.[b]	Found	Calcd.[b]	Found	
$(AA_{50}-EA_{32}-ES_8-DVB_{10})_1H$	7.70	5.21	—	—	1.64
$(AA_{50}-EA_{32}-ES_8-DVB_{10})_1h$	—	—	3.26	5.19	4.05
$(AA_{50}-EA_{32}-ES_8-DVB_{10})_1H+h$	7.70	5.21	4.02	3.26	—
$(AA_{60}-EA_{30}-MBAA_{10})H$	10.59	8.21	—	—	3.89
$(AA_{60}-EA_{30}-MBAA_{10})h$	—	—	3.05	5.15	14.92

[a] H = sample after the Hofmann degradation; h = sample after the alkaline hydrolysis.
[b] Calculated with eq. 1.

Figure 2. A characteristic band for the ethyl groups contained in EA and ethylstyrene at 2900–3000 cm^{-1}, a band at 1740 cm^{-1} assigned to C=O stretching from the ester groups, a strong band at 1665 cm^{-1} assigned to the stretching vibrations of the C=O bond from amide groups, an amide I band, and a band near 1170 cm^{-1}, which was found in the IR spectra both before and after the Hofmann degradation and was assigned to the C—N stretch, can be observed in the copolymer spectrum. A large band between 1550 and 1600 cm^{-1}, found after the alkaline hydrolysis of the ester groups, was assigned to carboxylate groups [Fig. 2(b)]. The
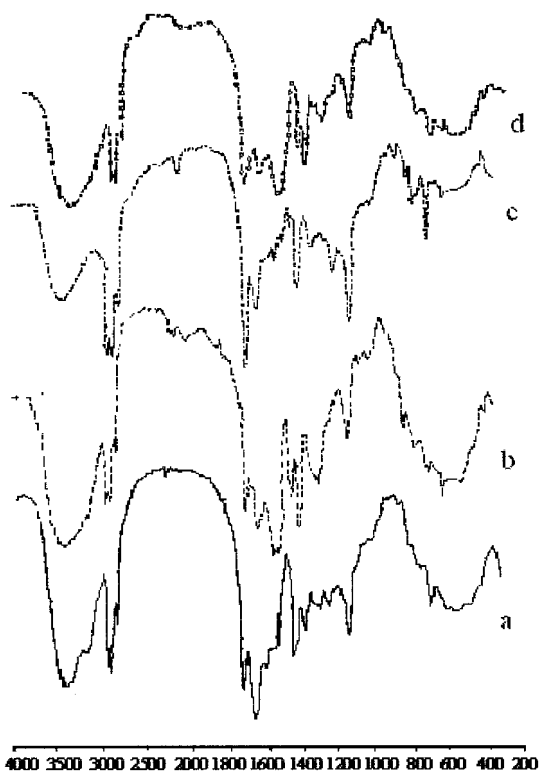

Figure 2 IR spectra of the starting $(AA_{50}-EA_{32}-ES_8-DVB_{10})_2$ copolymer and the derived ion exchangers: (a) the starting copolymer, (b) after the alkaline hydrolysis, (c) after the Hofmann degradation, and (d) alkaline hydrolysis performed after the Hofmann degradation.

characteristic band of the ethyl groups diminished but was still present because of the ethyl groups of ethylstyrene, which was also present as a comonomer. The band at 1320 cm^{-1}, which was shown after hydrolysis, was also assigned to the COO$^-$ groups. The band at 1665 cm^{-1} also diminished, and this showed that some of the amide groups were involved in this reaction and confirmed the results presented in Table II. After the Hofmann degradation [Fig. 2(c)], the bands at 2900–3000, 1740, and 1170 cm^{-1} increased in intensity, and the band characteristic of the C=O bond of the amide groups diminished but was still present. The characteristic band of the COO$^-$ groups, near 1570 cm^{-1}, which had to be present if the hydrolysis of the ester groups was significant as a secondary reaction,[5,7] was not found after the Hofmann degradation. This was evidence that the Hofmann degradation of the amide groups contained in the copolymers crosslinked with DVB was not accompanied by the formation of the COO$^-$ groups in a detectable amount. Figure 2(d) is characteristic of the amphoteric ion exchanger, which resulted from hydrolysis after the Hofmann degradation of the same AA copolymer.

The IR spectra of the $AA_{60}-EA_{30}-MBAA_{10}$ and $AA_{62}-EA_{30}-MBAA_8$ copolymers and the corresponding anion exchanger after the Hofmann degradation of $AA_{60}-EA_{30}-MBAA_{10}$ are shown in Figure 3. Spectra a and b are very similar to each other with respect to the characteristic bands because the difference between the starting copolymers was only 2 wt % MBAA (Table I). The strong band at 1670 cm^{-1} and the shoulder at 1740 cm^{-1} were assigned to the C=O bond of the amide groups, the amide I band, and the C=O bond of the ester groups, respectively. The band near 1170 cm^{-1}, assigned to the C—N stretching, was found in the IR spectra both before and after the Hofmann degradation. The characteristic bands of the amide group decreased in intensity after the Hoffman degradation of the amide groups contained in $AA_{60}-EA_{30}-MBAA_{10}$, but they were still present because of the MBAA used as a crosslinker. A new band with a low intensity was evident between 1560 and 1580
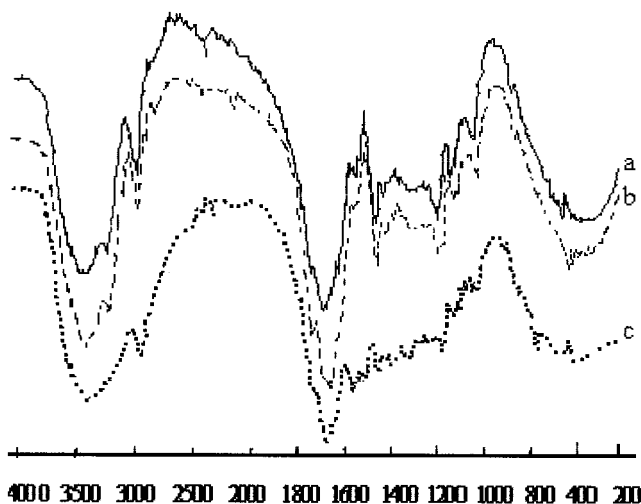
Figure 3 IR spectra of (a) the AA_{60}–EA_{30}–$MBAA_{10}$ copolymer, (b) the AA_{62}–EA_{30}–$MBAA_8$ copolymer, and (c) the AA_{60}–EA_{30}–$MBAA_{10}$ copolymer after the Hofmann degradation.

cm^{-1} and was assigned to the formation of the COO^- groups by the hydrolysis of some amide groups. This was proof of the specific influence of the crosslinker nature on the secondary reactions that could accompany the Hofmann degradation. This difference could be explained by the higher hydrophilicity of the AA copolymers crosslinked with MBAA in comparison with those crosslinked with DVB (Table II). The higher level of swelling and the higher flexibility of the chains between two crosslinks could create an environment similar to that existing in the Hofmann degradation of the amide groups from the AA homopolymer. This copolymer also had a higher density of amide groups, which could favor the secondary reaction.

Swelling data

Special techniques were developed to correlate the physical properties of the crosslinked copolymers with their structural parameters, such as the crosslink density and the molecular weight of a chain between two crosslinks. For this reason, the swelling phenomenon of crosslinked polymers, first time developed and studied by Flory,[14] has great importance. The swelling behavior of the AA crosslinked copolymers and the derived ion exchangers, in equilibrium with a pure solvent, was studied in water. A simplified technique was applied.[13,15] The calculation of the average molecular weight of a chain between two junctions was performed on the basis of swelling data in water with the following relationship:[16]

$$M_c = -V_l \rho_p \frac{(\phi^{1/3} - \phi/2)}{\ln(1 - \phi) + \phi + \chi_1 \phi^2} \qquad (2)$$

where M_c is the average molecular weight of the polymer between two junctions, V_1 is the solvent molar volume, ρ_p is the polymer skeletal density, and χ_1 is the Flory–Huggins interaction parameter. ϕ is the polymer volume fraction in the swollen state:

$$\frac{1}{\phi} = 1 + \left(1 + \frac{W_s}{W_p}\right)\frac{\rho_p}{\rho_s} \qquad (3)$$

where W_s is the weight of the swollen polymer, W_p is the weight of the dried polymer, and ρ_s is the density of the solvent used for swelling determinations (water).

The crosslink density (q) represents the molar fraction of the crosslinked units, which was estimated with the following equation:

$$q = (M_r/M_c) \times 10^2 \qquad (4)$$

where M_r is the average molecular weight of the polymer repeating unit. It was calculated with the following equation:

$$M_r = \sum f_i \times M_i \qquad (5)$$

where f_i is the molar fraction of the monofunctional monomers and M_i is the molar mass of the monofunctional monomers.

The theoretical average molecular weight between two crosslinks (M_{ct}) was calculated with the nominal crosslinking ratio of the molar fraction of the crosslinker to the molar fraction of the other comonomers (X):[17]

$$M_{ct} = 2M_r/X \qquad (6)$$

Some structural parameters, derived from the polymerization stoichiometry, are collected in Table III. Because water is not a good solvent for all segments of such copolymers, the swelling data of the starting AA copolymers and the derived ion exchangers were employed only to obtain relative information on the preservation of the crosslink density after the chemical transformations. The swelling results are summarized in Table IV. M_c, calculated with eqs. (2) and (3), first

TABLE III
Some Structural Parameters Calculated on the Basis of the Polymerization Stoichiometry

Sample	X	$M_r{}^a$	$M_{ct}{}^b$	q_t (%)[c]
$(AA_{50}$–EA_{32}–ES_8–$DVB_{10})_1$				
$(AA_{50}$–EA_{32}–ES_8–$DVB_{10})_2$	0.0709	77.39	2183	3.54
$(AA_{60}$–EA_{30}–$MBAA_{10})$	0.056	74.36	2656	2.79

[a] M_r was calculated with eq. (5).
[b] M_{ct} was calculated with eq. (6).
[c] q_t was calculated with eq. (4).

TABLE IV
Swelling Data in Water of the AA Starting Copolymers and the Ion Exchangers Derived on Their Basis

Sample	ρ_P	ϕ	χ_1	M_c	q (%)
$(AA_{50}–EA_{32}–ES_8–DVB_{10})_1$	1.1772	0.594	0.6155	127	72.4
$(AA_{50}–EA_{32}–ES_8–DVB_{10})_1H$	1.1772	0.581	0.5993	133	69.0
$(AA_{50}–EA_{32}–ES_8–DVB_{10})_2$	1.1216	0.602	0.5861	102	89.6
$(AA_{50}–EA_{32}–ES_8–DVB_{10})_2H$	1.1216	0.610	0.5730	92	99.0
$(AA_{60}–EA_{30}–MBAA_{10})$	1.0285	0.391	0.4855	322	23.0
$(AA_{60}–EA_{30}–MBAA_{10})H$	1.0285	0.256	0.1311	302	24.5
$(AA_{50}–EA_{32}–ES_8–DVB_{10})_2$ h	1.1216	0.247	0.5033	1700	5.4
$(AA_{60}–EA_{30}–MBAA_{10})h$	1.0285	0.067	0.1216	1506	4.9

revealed some qualitative information regarding the structures of the starting copolymers and the copolymers containing vinyl amine units after the Hofmann degradation. Therefore, for the same copolymer, the differences between the M_c values before and after Hofmann degradation were very small, this being evidence that the chemical transformation of the AA units into vinyl amine took place without significant changes in the initial crosslink density. If we compare the copolymers obtained with DVB as a crosslinker, we can see that M_c was a little higher for the $(AA_{50}–EA_{32}–ES_8–DVB_{10})_1$ copolymer, which was obtained with 1.3 wt % BPO, than for the $(AA_{50}–EA_{32}–ES_8–DVB_{10})_2$ copolymer synthesized with 1.5 wt % BPO. This shows a higher crosslinking efficiency with increasing BPO content. The highest M_c value was found for the copolymer synthesized with MBAA as a crosslinker at the same content in the initial mixture of monomers (10 wt %). This could be evidence for the influence of the crosslinker nature on the real crosslink density, the crosslinker content in the starting monomer mixture being the same.

For the cation exchangers obtained by the hydrolysis reaction of the ester groups, the differences between the theoretical and experimental values of M_c and q were low (Tables III and IV). Both $(AA_{50}–EA_{32}–ES_8–DVB_{10})_2h$ and $(AA_{60}–EA_{30}–MBAA_{10})h$, containing carboxylic groups, showed high hydrophilicity (Table II). These results were especially important for the cation exchangers derived from the hydrolysis of the ester groups contained in the $AA_{60}–EA_{30}–MBAA_{10}$ copolymer and showed that MBAA was not involved in the hydrolysis reaction. Also, the good agreement between the calculated and experimental values of the structural parameters, for the last samples, was evidenced for the first time for such copolymers.

TGA

The AA crosslinked copolymers and the ion exchangers obtained from them were also characterized by dynamic thermogravimetry (TG) and derivative thermogravimetry (DTG). TG and DTG curves, character-

istic of the $(AA_{50}–EA_{32}–ES_8–DVB_{10})_2$ copolymer and the derived ion exchangers, are presented in Figure 4. The characteristic temperatures and the weight losses of the main decomposition step are collected in Table V. A detailed thermogravimetric study of the starting AA copolymers and the corresponding ion exchangers, with respect to the structural parameters, has been published elsewhere.[18]

All the copolymers presented four decomposition steps. The third decomposition stage, considered the main stage of thermodegradation for all the samples, was characterized by the highest weight-loss values as
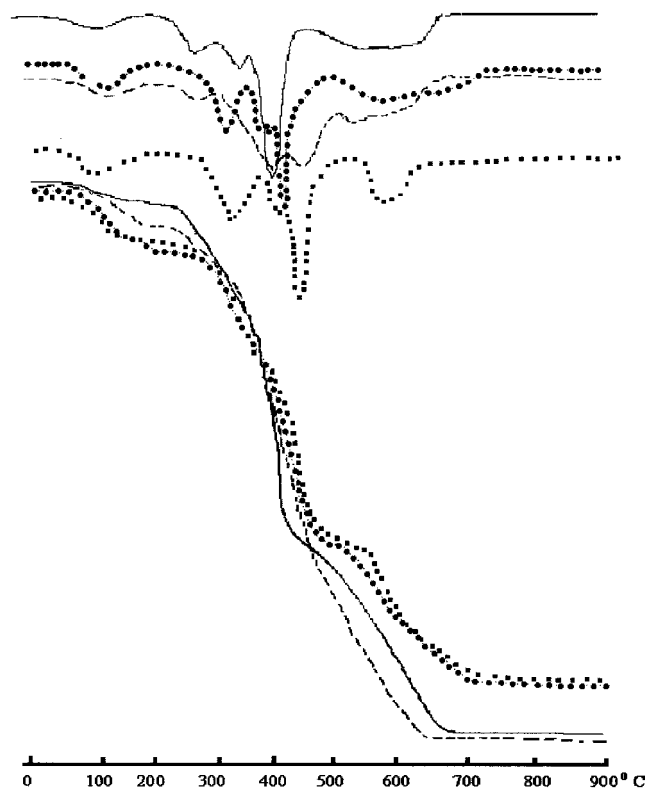

Figure 4 TG and DTG curves of the starting $(AA_{50}–EA_{32}–ES_8–DVB_{10})_2$ copolymer and the derived ion exchangers: (—) $(AA_{50}–EA_{32}–ES_8–DVB_{10})_2$, (–) $(AA_{50}–EA_{32}–ES_8–DVB_{10})_2H$, (●) $(AA_{50}–EA_{32}–ES_8–DVB_{10})_2h$, and (■) $(AA_{50}–EA_{32}–ES_8–DVB_{10})_2H+h$.

TABLE V
TGA Results of the Starting $(AA_{50}-EA_{32}-EA_8-DVB_{10})_2$ Copolymer and the Derived Ion Exchangers

Sample	T_i[a]	T_m[b]	T_f[c]	Weight loss (%)
$(AA_{50}-EA_{32}-EA_8-DVB_{10})_2$	305	400	450	48
$(AA_{50}-EA_{32}-EA_8-DVB_{10})_2H$	260	380	450	54
$(AA_{50}-EA_{32}-EA_8-DVB_{10})_2h$	340	425	490	35
$(AA_{50}-EA_{32}-EA_8-DVB_{10})_2H+h$	355	435	495	31

[a] Initial decomposition temperature (°C).
[b] The temperature corresponding to the maximum rate of decomposition (°C).
[c] The final decomposition temperature (°C).

follows: 48 wt % for the starting copolymer, 54 wt % for the anion exchanger with primary amine groups, 35 wt % for the cation exchanger with carboxylate groups, and 31 wt % for the amphoteric ion exchanger. The T_m values (see Table V) were in the following order: 380°C for the anion exchanger, 400°C for the starting copolymer, 425°C for the cation exchanger, and 425°C for the amphoteric ion exchanger. Both the weight-loss and T_m values showed that the anion exchanger had the lowest thermal stability, and the highest thermal stability was proper for the amphoteric ion exchanger. As can be seen from Figure 4, the char yield also increased for $(AA_{50}-EA_{32}-ES_8-DVB_{10})_2h$ and $(AA_{50}-EA_{32}-ES_8-DVB_{10})_2H+h$. This behavior was expected because of the presence of Na as a counterion in the cation structure.

CONCLUSIONS

With this study on the synthesis and characterization of some ion exchangers derived from crosslinked copolymers of AA and EA, we showed that both anion exchangers, by the Hofmann degradation of the amide groups, and cation exchangers, by the alkaline hydrolysis of the ester groups, could be obtained from the same copolymer. The main functional groups of the ion exchangers were evidenced by IR spectroscopy, ion-exchange-capacity measurements, and TG. The correlation between the AA crosslinked copolymer structure and the structural changes observed after the chemical reactions of these copolymers was demonstrated. Therefore, the structure of the copolymer after the Hofmann degradation contained AA units in addition to the vinyl amine units, and some of the amide groups were transformed into carboxylate groups af-

ter the alkaline hydrolysis of the ester groups. The hydrolysis of the amide groups as a secondary reaction, in addition to the Hofmann degradation, was evidenced mainly when MBAA was used as a crosslinker. Swelling data in water gave qualitative information on the crosslink density before and after the chemical reactions of the crosslinked copolymers.

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