Synthesis and Characterization of Poly(acryloxyethyl-trimethylammonium chloride-*co*-2-hydroxyethyl methacrylate): A Study of its Interaction with Sodium Alginate

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ABSTRACT: Poly(acryloxyethyl-trimethylammonium chloride-*co*-2-hydroxyethyl methacrylate) [poly(Q-*co*-H)] was prepared by free radical polymerization in aqueous solution at 60°C using potassium persulfate as initiator. Spectroscopic characterization confirmed the formation of poly(Q-*co*-H) and the molar fractions of acryloxyethyl-trimethylammonium chloride monomer units incorporated in the copolymers were determined by potenciometric titrations. The monomer reactivity ratios for Q and H are found to be $r_Q = 0.04 \pm 0.01$ and $r_H = 3.22 \pm 0.84$ using Fineman–Röss method and $r_Q = 0.06$ and $r_H = 3.61$ using Genetic Algorithms method. Finally we studied reaction between poly(Q-*co*-H) and sodium alginate by conductimetric measurement. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1680–1688, 2008

Key words: acryloxyethyl-trimethylammonium chloride; reactivity ratio; interpolymeric complexes

INTRODUCTION

The design and preparation of interpolymeric complexes for biomedical applications are one of the most interesting fields of research for new polymeric systems such as biomaterials, mainly after the Ringsdorf's report of a practical model for active polymeric systems.

Polyelectrolyte complexes result from the interaction of macromolecules carrying electrostatic complementary ionizable groups. These have been proposed as suitable for drug delivery systems, proteins and materials separation, anticoagulant coating, and even as skin substitutes. Most of the literature related with the preparation of polyelectrolyte complexes reports the use of natural polyelectrolyte, generally polysaccharides or their derivatives. Hence, the challenge of gaining a better understanding of the underlying mechanism that controls these complexes prompted us to focus on hybrid systems based on polyelectrolytes both of natural and synthetic source. In this work we report the preparation of a novel polyelectrolyte complex prepared by copolymerization of 2-hydroxyethyl methacrylate and acryloxyethyl-trimethylammonium chloride.

Because of its anionic character, sodium alginate has received increasing attention as a polymeric component in a wide variety of such complexes, though its copolymer based in acryloxyethyl-trimethylammonium chloride has not been studied within this field.

Reactions between polyelectrolyte are accompanied by releasing ionic species with different mobility to the reaction medium, what makes conductometry a useful technique to study these processes. Unfortunately, very few reports are found on this subject despite of the relevant information that may be obtained through its implementation. This may be due to the careful procedures that must be followed, including meticulous purification of the polymer.

The copolymer characterization was carried out using spectroscopic and potenciometric techniques. Moreover, a new procedure for the calculation of r_1 (r_Q) and r_2 (r_H) based on random techniques for parameter estimation is presented and applied to
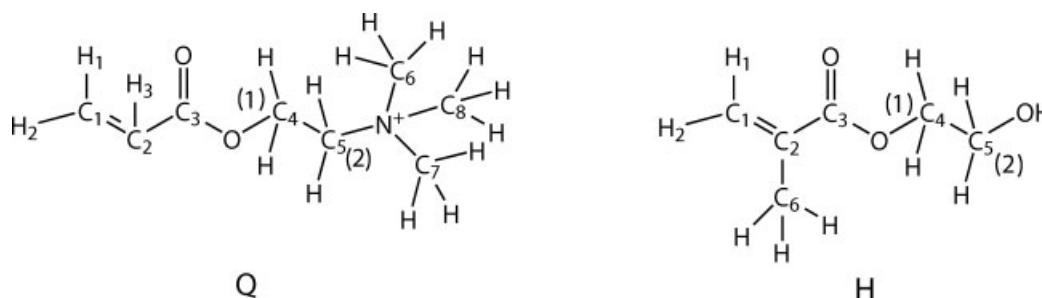
Figure 1 Chemical structure of the monomer unit.

know the fitness of the reactivity ratios for acryloxy-ethyl-trimethylammonium chloride/2-hydroxyethyl methacrylate copolymerization system. The values of the reactivity ratios thus obtained were used to calculate the microstructural parameters of the copolymers.

The sodium alginate characterization was carried out using spectroscopic techniques. Also, the complex formation was evaluated using conductimetric measurement.

MATERIALS AND METHODS

Materials

2-Hydroxyethyl methacrylate (H, Merck), acryloxy-ethyl-trimethylammonium chloride (Q, AQUATECH)

(Fig. 1), potassium persulfate ($K_2S_2O_8$, Fluka; 0.001%N), acetonitrile (CH_3CN, Merck), and silver nitrate ($AgNO_3$, Merck) were used as received.

Sodium alginate obtained from yellow powder was purchased from SIGMA Chemical Co. Its viscosity average molar mass was 3.83×10^4 g/mol, which was determined by viscometry in $0.2M$ NaCl at 25°C. The polysaccharide samples were carefully purified prior to use. Twice distilled water ($\sigma = 1.3$ μS/cm) was employed during the experiments. All other reagents were of extra pure grade and used as purchased.

The polymerization of the poly(acryloxyethyl-trimethylammonium chloride-*co*-2-hydroxyethyl methacrylate) and the formation of the interpolymer complex with the sodium alginate are described in Scheme 1.
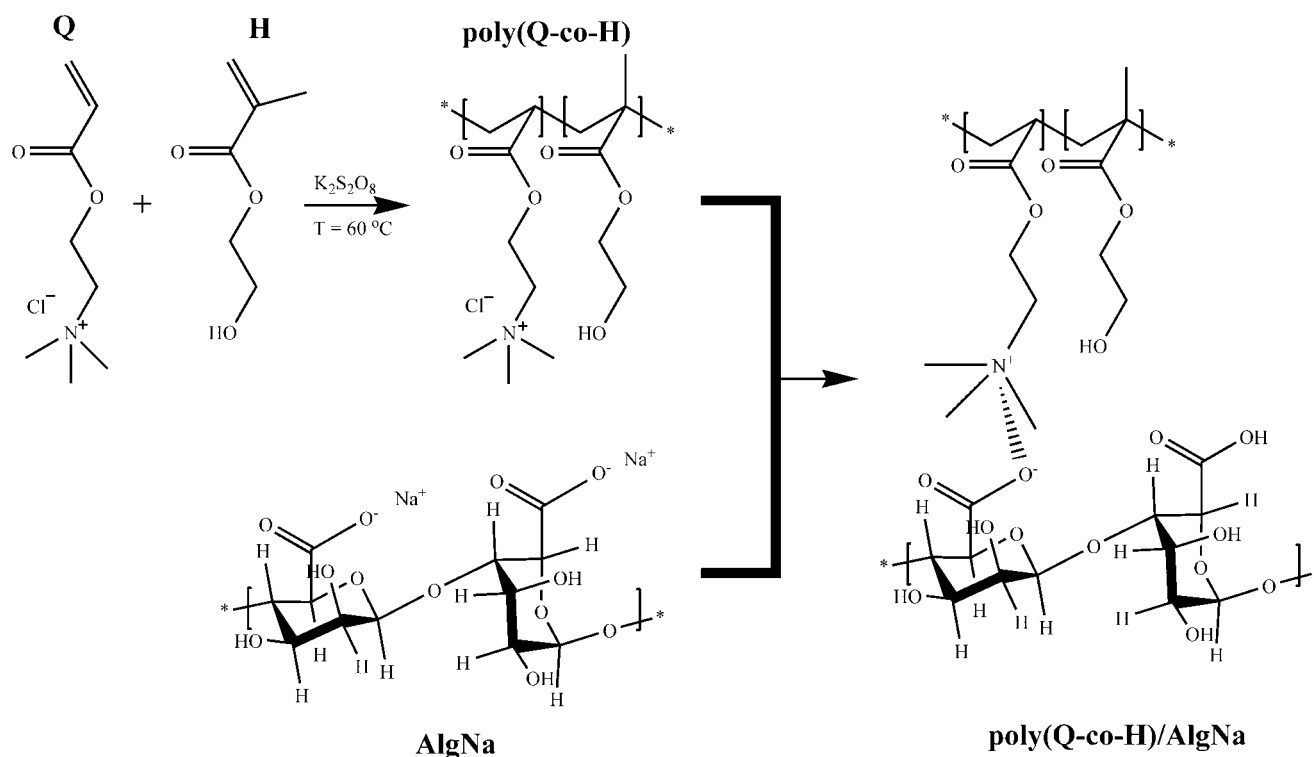
Scheme 1

Methods

Copolymerization

Poly(acryloxyethyl-trimethylammonium chloride-*co*-2-hydroxyethyl methacrylate) was prepared by free radical polymerization of the corresponding monomers (i.e., Q and H) in water solution at 60°C, and was using $K_2S_2O_8$ as initiator in Pyrex glass flask under nitrogen atmosphere. Comonomer and initiator concentrations were 1.0 and 0.01 mol/L, respectively. After the proper reaction time, the flask content was poured into a large excess of acetonitrile. The precipitated copolymer was rotoevaporated to separate the acetonitrile and was dried under vacuum until constant weight was attained.

Spectroscopic experiments

The copolymers were characterized by ^{1}H/^{13}C NMR spectroscopy. Alginate was characterized by infrared spectroscopy. IR spectra of sodium alginate were recorded in KBr pellets on an FTIR ATI-MANSON Spectrometer with 4000–400 cm^{-1} spectral interval. NMR spectra were recorded with a Bruker AC-250F spectrometer, equipped with an ASPECT 3000 computer, at 250 MHz (^{1}H) and 62.89 MHz (^{13}C) frequencies at 30°C. Monomers and copolymers were dissolved in deuterium water ($c = 10$ mg/mL). Tetramethylsilane (TMS) was used as internal reference and chemical shifts are reported in parts per million. All commercially available chemicals were used without further purification.

Polymer composition

The molar fractions of acryloxyethyl-trimethylammonium chloride monomer units incorporated in the copolymers were determined by potenciometric titrations. The potenciometric measurements were recorded with magnetic agitation at, 25°C, in a CRISON potenciometer. It used a silver electrode been accustomed to as analytic sensor.

Purification of sodium alginate

An aqueous solution of sodium alginate (5 g/L) was successively filtered through sintered glass filter (pore diameters: 2, 3, 4, and 5) and membranes (0.80 and 0.45 μm). The polysaccharide was precipitated by gradual addition of saturated ethanol until a final 70% (v/v) alcohol concentration was attained. The solid was separated by filtration and was dried under vacuum at 45°C for 24 h. Finally the purified

polymer was dried at 25°C for another 24 h in a suitable incubator.

Conductimetric measurements

Conductimetric experiments were carried out in glass cell at 25°C ± 1°C. A digital CRISON equipment was used. The experiments were always performed valuing the sodium alginate solutions (5.3×10^{-4} mol/L) with the poly(acryloxyethyl-trimethylammonium chloride-*co*-2-hydroxyethyl methacrylate) solutions (5.3×10^{-3} mol/L). We should point out that the concentrations are referred in particular to the molar mass of the equivalent one for each case. The pH-values of the polyelectrolyte solutions were those of the starting solutions.

Genetic algorithms

We have applied evolutionary algorithms to estimate the values of the reactivity ratios (i.e., r_Q and r_H) by following a genetic algorithm (GA) approach.[1]

Four different computational simulations with GAs (GA1, GA2, GA3, and GA4) were run. Populations of potential solutions (i.e., potential pairs of reactivity ratios for the copolymerization system in study) comprised 100 uniformly distributed individuals. Initial populations were generated by using the Mersenne–Twister pseudo random number generator.[2] Genetic operations and the selection of individuals were performed according to the settings described by Monett et al.[3]

The main difference among all simulations was in the definition of the intervals for the reactivity ratios: for each simulation (e.g., GA4) suitable intervals were defined according to the fittest individuals from former simulations (e.g., GA3). In the first simulation (i.e., GA1) the stop criterion was set to a value less than the Euclidean distance ψ [eq. (1)] calculated with the solution obtained with the Fineman–Röss method[4] applied to the same copolymerization system.

$$\psi = \sqrt{\sum_{i=1}^{m} \left(F_i^{\text{pred}} - F_i^{\text{obs}} \right)^2} \qquad (1)$$

where m is the number of experimental measurements over time, F^{pred} are the predicted data (e.g., calculated by GAs), and F^{obs} are the experimental measurements of monomer compositions in copolymer.

The performance of the GAs was evaluated on a Sun Ultra 5/10 computer with an UltraSPARC-IIi 400 MHz processor, 131,072 Kb of RAM, and SunOS Release 5.6 Version Generic-105181-19 operating system.

TABLE I
^{1}H and ^{13}C Chemical shifts, δ (ppm), and Signal Assignments of Q and H in D$_2$O

	^{1}H NMR	δ (ppm)	^{13}C NMR	δ (ppm)
Acryloxyethyl-trimethylammonium chloride (Q)	H$_1$	6.32	C$_1$	134.58
	H$_2$	6.05	C$_2$	128.27
	H$_3$	6.10	C$_3$	168.50
	CH$_2$ (1)	3.85	C$_4$	59.73
	CH$_2$ (2)	4.78	C$_5$	65.84
	(CH$_3$)$_3$	3.28	C$_6$, C$_7$, C$_8$	55.12
2-Hydroxyethyl methacrylate (H)	H$_1$	5.65	C$_1$	128.18
	H$_2$	6.12	C$_2$	136.97
	CH$_3$	1.92	C$_3$	170.94
	CH$_2$ (1)	4.22	C$_4$	67.54
	CH$_2$ (2)	3.81	C$_5$	60.78
	OH	4.75	C$_6$	18.61

RESULTS AND DISCUSSION

Spectroscopic characterization of monomers, copolymer and the sodium alginate

The characteristic of monomers define the copolymers properties. Therefore, it is very important the characterization of the monomers before the copolymer formation starts.

The monomers were characterized by ^{1}H and ^{13}C NMR spectroscopy. Both samples were investigated under similar conditions, and hydrogen and carbon. The chemical shift and signals assignment of the ^{1}H and ^{13}C NMR spectra are summarized in Table I for both monomers. Comparing the spectra of analogous chemical groups taken from the literature.[5]

All the resonance signals have been assigned to the corresponding atoms according to the chemicals structures drawn in Figure 1.

After characterization of the starting monomers, syntheses at low and high conversion were carried out to sweep a wide range of compositions (0–100% of Q). However, the system (Q/H) presents a characteristic behavior under the employed conditions, which was not achieved before it was exposed since when surpassing 30% of H in the feeding mixture as a reactive, the samples gelified.

This behavior can be associated to the quality of the 2-hydroxyethyl methacrylate used. The commercial 2-hydroxyethyl methacrylate comes impure with ethyleneglycol dimethacrylate (EDMA), a bifunctional monomer that can cause crosslinker action during the copolymer synthesis. This impurity has a lower concentration resulting in an impossible spectroscopic determination. However, this concentration is enough to create crosslinking.[6] Besides, in the H structure a hydroxyl is present, which allows a transfer by the labile hydrogen. In other words, in the propagation stage one radical for each the vinylic and the hydroxyl links are formed. These evidences might be conferred to the 2-hydroxyethyl methacrylate's crosslinker properties that act in a competitive way.

Figure 2 shows the chemical structure of poly-(acryloxyethyl-trimethylammonium chloride-*co*-2-hydroxyethyl methacrylate) and the ^{1}H NMR and ^{13}C NMR spectra. Disappearance of the signals corresponding to the vinylic protons of both monomers is observed on the ^{1}H NMR spectrum.

On the other hand, the ^{13}C NMR spectrum offers similar information. This spectrum is characterized by the disappearance of the vinylics signs of both monomers and the appearance of a sign in 45.92 ppm that it corresponds at the CH$_2$ groups of the skeleton of the polymeric chain. The chemical shift and signal-assignment of the ^{1}H and ^{13}C NMR spectra are show in Figure 2.
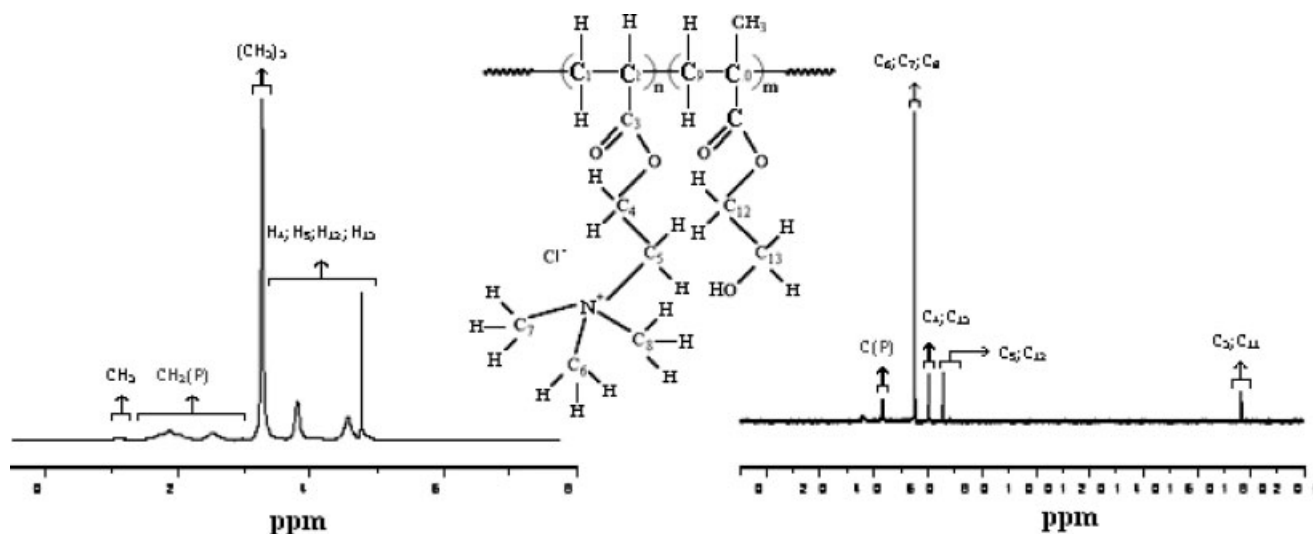

Figure 2 Chemical structure of poly(Q-*co*-H) and ^{1}H, ^{13}C NMR spectrum (F_1 = 0.50).

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TABLE II
Infrared Frequencies (cm⁻¹) and Band Assignments
of Sodium Alginate Infrared Spectrum

Band			
ν (cm^{-1})	Assignments	Alg-Na	Alg-Na (standard)
3400–3200	ν_{OH}	3454–3202	3422
2920–2900	ν_{Csp^3-H}	2900	2940–2900
1650–1550	$\nu_{C=O}$	1607	1613
1300–1000	ν_{C-O-C}	1240	1250
1420, 1300–1200	$\nu^{as}_{C-O} + \delta_{CH}$	1413, 1300	1416, 1320
1000–650	γ_{OH}	910	903

Table II summarizes the fundamental infrared frequencies and band assignments for sodium alginate (Fig. 3). The signs obtained was compared with a patron sample of sodium alginate.[7] In the sodium alginate infrared spectra the region stood among 3454–3202 cm^{-1}, which is the widest and intense sign in the characteristic spectrum of the acids that appear. In 1607 cm^{-1} the most intense sign in the spectrum appears that have been assigned to the frequency of the C=O vibration. The position of this band is adjusted to the range reported in the literature for this functional group in polysaccharides. Another very intense sign that is reported is the one that the one appears in the 1240 cm^{-1} which this assigned to the valency frequency ν_{C-O-C}.

Evaluation of reactivity ratios

The copolymerizations of 2-hydroxyethyl methacrylate with acryloxyethyl-trimethylammonium chloride in aqueous solutions were studied in a wide composition interval with molar fractions of Q ranging from 0.92 to 0.60 in the monomer feed. The reaction time was initially regulated to reach conversions lower than 5 wt %, to satisfy the differential copolymerization equation for the low conversion. The molar fraction of monomers units incorporated in the copolymers was determined from the potenciometric analysis of copolymers samples prepared with different monomer feeds.

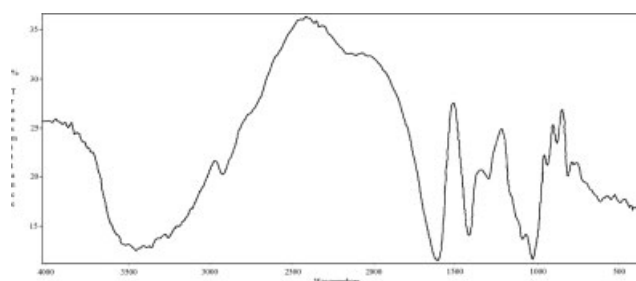Experimental measurements for the poly(acryloxyethyl-trimethylammonium chloride-*co*-2-hydroxyethyl

Figure 3   IR spectrum of sodium alginate.

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TABLE III
Composition and Conditional Probability Data of the
Free Radical Copolymerization of Q and H

Feed f_Q	Copolymer F_Q	Conversion (wt %)	P_{QH}	P_{HQ}
0.92	0.53	6.0	0.592	0.762
0.85	0.50	5.0	0.746	0.612
0.79	0.41	4.4	0.816	0.511
0.72	0.36	3.4	0.866	0.417
0.67	0.27	3.0	0.891	0.361
0.60	0.19	2.6	0.917	0.294

methacrylate) copolymerization system are reported in Table III. Composition data with respect to monomer Q for the feed (i.e., f_1 from first column) and copolymer (i.e., F_1 from second column) are summarized.

The classical copolymerization model describes the relative change in monomer concentrations ($d[M_1]/d[M_2]$) as a function of the instantaneous monomer concentrations, $[M_1]$ and $[M_2]$, and the monomer reactivity ratios, r_1 and r_2, by means of the general copolymerization equation. The reactivity ratios of the monomers were determined according to this equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (2)$$

Initial approximated values of r_Q and r_H for the GA simulations were obtained by applying the Fineman–Röss linearization method:

$$\frac{f_M(1 - 2F_M)}{F_M(1 - 2f_M)} = r_M \frac{f_M^2(F_M - 1)}{F_M(1 - f_M)^2} + r_p \quad (3)$$

where F refers to the composition in the copolymer and f refers to the composition in the feed, both according to the principal monomer (i.e., Q).

The scores presented in Table IV correspond to the four different estimations for r_Q and r_H (columns 2 and 3, respectively) by using GAs. These estimations are sorted from less (GA1) to more adjusted (GA4). The most reliable reactivity ratios were found to be close to 1 for both comonomers, which means that the monomers distribution in the copolymer is expected to be mainly alternate and that the reaction is not far from the ideal copolymerization.

Error estimations by using different numerical criteria are reported in Table V. The quality of the solutions can be assessed, for example, by comparing the values of the Euclidean distance (i.e.,ψ) for each case. As observable from the table, the application of GAs decreases the Euclidean distances between theoretical and experimental data when varying the genetic parameters: higher-quality solutions are identified with GA4, being 9.20439×10^{-2} the smaller and most representative value of ψ. Note that this

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TABLE IV
Calculated Reactivity Ratios for the Composition Data
of the Poly(Q-*co*-H) Copolymerization system

Method	Reactivity ratios				
	r_Q	r_H	$r_Q r_H$	$1/r_Q$	$1/r_H$
Fineman–Röss	0.04 ± 0.01	3.22 ± 0.84	0.13	25	0.3
GA 1 (6)[a]	0.0591424	3.52545	0.20850	16.90834	0.28365
GA 2 (9)	0.0646260	3.63275	0.23477	15.47365	0.27527
GA 3 (4)	0.0629767	3.60910	0.22729	15.87889	0.27708
GA 4 (1209)	0.0629371	3.60972	0.22719	15.88888	0.27703

[a] The number of GA iterations where the best values were achieved are given in parenthesis.

value, by applying the Fineman–Röss method, is far away from the obtained by GAs. Thus, we can suggest the estimations for the reactivity ratios obtained with GA4 (approx. $r_Q = 0.063$ and $r_H = 3.61$) as the most probable values for poly(acryloxyethyl-trimethyl-ammonium chloride-*co*-2-hydroxyethyl methacrylate) copolymerization system. As in previous work,[8] the accurate determination of reactivity ratios by GAs demonstrates the advantages in using evolutionary techniques to this kind of real problem.

Theoretical values for the copolymer compositions (i.e., F_1' and F_1'') when used the estimations obtained with GA4 are reported in Table VI. These values were obtained by substituting the estimations for the reactivity ratios in the copolymer composition equation for each value from the feed.

The average composition diagram shown in Figure 4 has been drawn with the GA4 r_Q and r_H values when applying the general copolymerization equation[9] [eq. (1)]; the experimental composition data adequately fit the theoretical diagram, which is represented by a solid line.

The reactivity of growing radicals with Q ends, as measured by the ratio $1/r_Q$, and the reactivity of the growing radicals with H ends, as measured by the ratio $1/r_H$, is rather similar towards both monomers. Besides, the product $r_Q \cdot r_H$ is near to zero indicating that the system does not behave closed to the ideal one.

From the values of the reactivity ratios r_Q and r_H given in Table IV and taking into account well known statistical relationships, we have determined the run number, R, defined by Ritchey and Ritchey[10] as the average number of monomers alternations in a copolymer per 100 monomeric units. This parameter provides a useful picture of the sequence distribution in a copolymer chain and can be used to estimate the variation of the physical properties of copolymers with the composition. Values of R have been determined in terms of reactivity ratios and probability statistics for different values of the molar fraction of Q in the feed.

The maximum value of R, when $R = 67$, is reached for a Q molar fraction in the feed of about 5.66 as shown in Figure 5.

The statistical distribution of Q centered triads were determined considering the equations for the first order Markovian transition probabilities P_{QH}, P_{HQ} P_{QQ}, and P_{HH} as follows:

$$P_{QH} = 1 - P_{QQ} = \frac{1}{1 + r_Q X} \quad (4)$$

$$P_{HQ} = 1 - P_{HH} = \frac{1}{1 + r_H/X} \quad (5)$$

where $X = [Q]/[H]$ represents the ratio of the concentration of Q and H in the monomer feed. Figure 6

TABLE V
Error Estimations by Different Numerical Criteria for the Poly(Q-*co*-H)
Copolymerization System

Method	Criterion		
	l_2-Norm[a]	Euclidean distance[b]	Quadratic mean deviation[c]
Fineman–Röss	–	–	–
GA1	8.50656×10^{-3}	9.22310×10^{-2}	1.41776×10^{-3}
GA2	8.50233×10^{-3}	9.22081×10^{-2}	1.41706×10^{-3}
GA3	8.47210×10^{-3}	9.20440×10^{-2}	1.41202×10^{-3}
GA4	8.47208×10^{-3}	9.20439×10^{-2}	1.41201×10^{-3}

[a] l_2-Norm $= \psi^2$.
[b] l_2-Norm$^{1/2} = \psi$.
[c] l_2-Norm$/m = \psi^2/m$, where m is the number of experimental data.

TABLE VI
Theoretic Values When Using the Estimated Reactivity Ratios from GA4

Feed f_1	Copolymer F_1	GA4[a] F_1'	GA4[b] F_1''
0.92	0.53	0.567468	0.567566
0.85	0.50	0.453173	0.453231
0.79	0.41	0.386935	0.386971
0.72	0.36	0.325845	0.325865
0.67	0.27	0.288752	0.288766
0.60	0.19	0.243153	0.243159

[a] Copolymer compositions without considering approximated values for r_1 and r_2.
[b] Copolymer compositions by considering approximated values for r_1 and r_2 (with three and two places after the comma, respectively.

shows the diagrams of the statistical distribution of Q centered triads along the copolymer chains, as function of the ratio of molar concentration of both monomers in the feed.

As it is expected, as X increases, the HQH triad molar fraction decreases smoothly where as the molar fraction of homotriads QQQ increases. This happens because, when X increases, the quantity of Q increases having more tendencies to homopolymerization. On the other hand, the molar fraction of heterotriads with one Q unit, i.e., $HHQ^+ = HHQ + QHH$, increases while X increases, which can be explained by the growth in the Q concentration.

Determination of the copolymer composition by potenciometric analysis

Resulting properties of a copolymer such as deformability, hidrofobicity, biocompatibility, porosity, insolubility, etc. will highly depend on the relationship that exists between the monomers. Thus, the determination of the real composition of the copolymer was very important in this work.

There are different techniques to know the microstructure of a polymer like the ^1H, the ^{13}C NMR, and the infrared spectroscopy, among others. In the
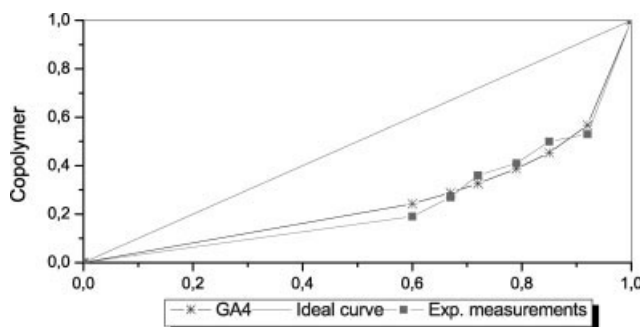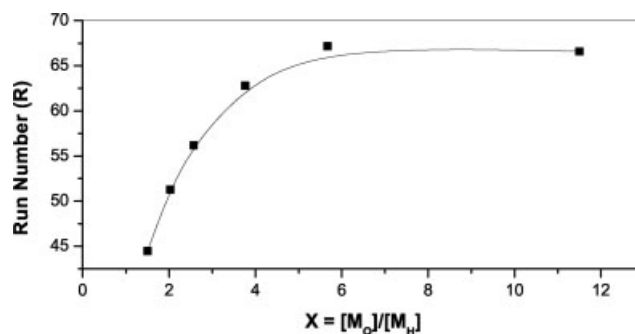
Figure 5 Variation of the Run Number, R, of monomers with monomers concentration, X, in the feed.

case that concerns us, the structure of the Q molecule contained chloride ions. This allowed us to carry out a potenciometric tritation and, with it, to determine the composition of Q in the copolymer. During the course of the potenciometric tritation the formation of one precipitate of silver chloride (AgCl) tooks place (Scheme 2).

The titration reaction stoichiometric was 1 : 1, i.e., there will be so many Cl^- as Ag^+ ions in the equivalence point. Therefore, to determine the mass of Q, it was only necessary to know the volume of silver nitrate used in the final point of the titration. This was determined by calculating the first derivatives in the resulting potenciometric curves. Table VII reports the obtained results by both high and low conversions. Such results show that the copolymer obtained from the synthesis is formed by Q and H. In addition, the content of Q in the original mixture increases as the volume of used silver nitrate increases.

Conductimetric analysis of the reaction between sodium alginate and poly(acryloxyethyl-trimethylammonium chloride-*co*-2-hydroxyethyl methacrylate)

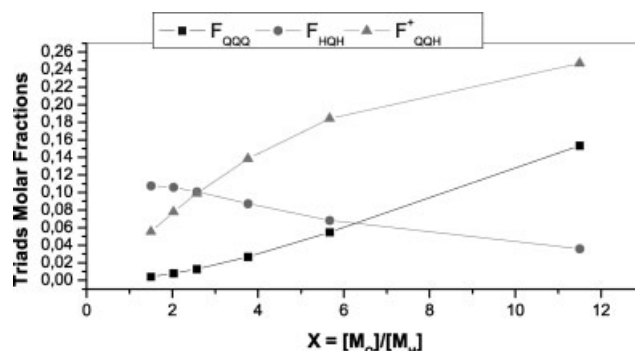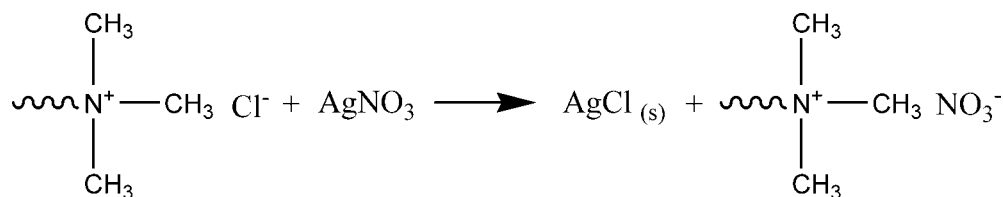One of the major purposes of this work is to investigate the complex formed between oppositely

Figure 4 Average composition diagram using Q as principal monomer.

Figure 6 Variation of molar fraction of Q centered triads with the ratio of monomers concentration, X, in feed.

Scheme 2

charged polyelectrolytes by using conductivity measurement, because this reaction is accompanied by the release of ionic species (in our case NaCl) with different mobilities to the medium. The interpolyelectrolyte interaction when sodium alginate reacts with poly(acryloxyethyl-trimethylammonium chloride-co-2-hydroxyethyl methacrylate) could be represented as in Scheme 1.

At the beginning of the reaction, the dissolutions for both polyelectrolytes were colorless. Elapsed some time, such dissolutions become turbid evidencing the formation of a precipitate, which corresponds to the interpolymeric complex poly(Q-co-H)/NaAlg.

Figure 7 shows the behavior of the conductivity of the reaction mixture as a function of the molar fraction of the reaction system, Z (i.e., poly(Q-co-H)/NaAlg), during the formation of the polyelectrolyte complex when poly(acryloxyethyl-trimethylammonium chloride-co-2-hydroxy-ethyl methacrylate) solution is added to a solution of NaAlg. As the value of Z increases a slight and monotonic increment in the slope of the conductivity curve until 0.7 could be appreciated. At this point a little slope change is observed, which is attributed to the probable hydrolysis of the forming interpolymeric complex (Scheme 3). Nevertheless, the value of the slope is not very high as it should be expected in the liberation of hydroxyl ions (OH^-). This is due to the consumption of these ions with the course of the reaction, as a result of the equilibrium displacement represented in Scheme 3. After the equivalence point is reached, a change in the slope of the conductivity curve is observed, indicating that the formation of

the interpolymeric complex has been completed, and an excess of NaAlg begins to appear in the reaction medium.

At the equivalence point it was estimated that Z ([Q-H]/[NaAlg]) (1.0. This value of Z indicates the formation of a complex with 1 : 1 stoichiometric, which means that, for each carboxyl group that is present in the sodium alginate structure, there is an amino quaternary group of the copolymer that reacts.

Potenciometric measurements simultaneously carried out in our laboratory have shown that the pH of the reaction medium does not change appreciably during the addition of poly(acryloxyethyl-trimethylammonium chloride-co-2-hydroxyethyl methacrylate) to NaAlg until values of Z are close to unity. Indeed, the value of the pH varies from 6.74 at $Z = 0$ to
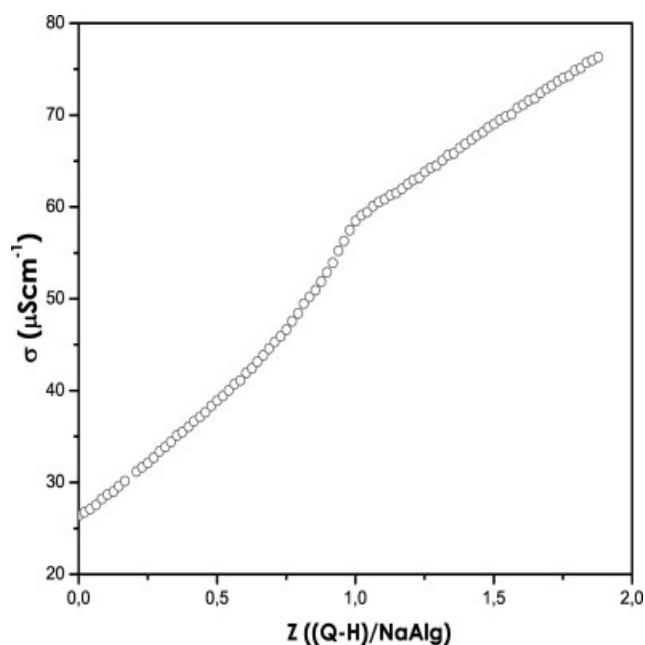

Figure 7 Conductimetric curve corresponding to the addition of poly(acryloxyethyl-trimethylammonium chloride-co-2-hydroxyethyl methacrylate) solution to that of sodium alginate as a function of the molar fraction of the reaction system, Z ([poly(Q-co-H)]/[NaAlg]). Experimental points in the vicinity of the equivalence point are shown enhanced. The values of the specific conductivity have been corrected to take into account the dilution during the gradual addition of the solution.

TABLE VII
Data Obtained in the Titration of the Synthesized Copolymer to Low and High Conversion Using Silver Nitrate (M: Copolymer compositions used; m_1: Copolymer mass; m_2: Obtained mass of Q)

M	Low conversion		High conversion	
	m_1 (g)	m_2 (g)	m_1 (g)	m_2 (g)
95/5	0.3	0.19	3.85	3.79
90/10	0.25	0.12	3.28	3.17
85/15	0.22	0.10	3.00	2.90
80/20	0.17	0.09	2.78	2.63
75/25	0.15	0.08	2.48	2.28
70/30	0.13	0.03	2.06	1.74
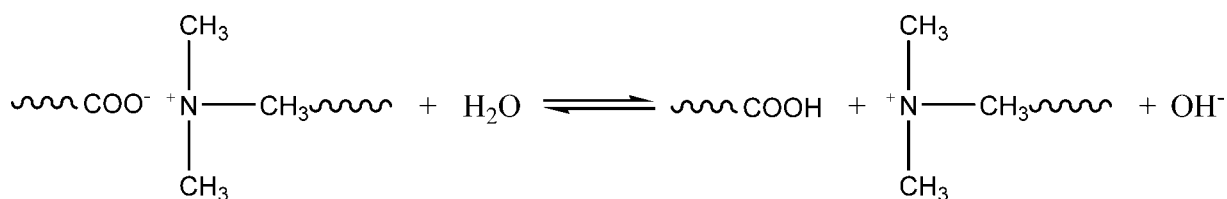
Scheme 3

approximately 7.02 at Z slightly higher than 0.9. Then it could be considered that during the formation of the interpolyelectrolyte complex the polyacid is almost fully ionized.

The slope values and the volumes used for each composition of the copolymer results allowed us to conclude that, as the quantity of Q that is present in the copolymer increases, the charge concentration also increases. As a consequence, less copolymer volume is needed to satisfy the same quantity of opposed charges that result from the sodium alginate. Furthermore, the conductivity of the means increases proportionally according to the charge density that exists on it, corroborating previous results obtained by potenciometric analysis.

CONCLUSIONS

Our results shows that the reactivity ratios of Q/H copolymer system are found to be $r_Q = 0.06$ and $r_H = 3.61$. The study of the reaction between synthetic and natural macromolecules indicates the formation of complex polyelectrolyte with stechiometry 1 : 1.

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