

Hydrosoluble Copolymers of Acrylamide-(2-acrylamido-2-methylpropanesulfonic acid). Synthesis and Characterization by Spectroscopy and Viscometry

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ABSTRACT: Hydrosoluble copolymers containing sulfonic acid groups incorporated into a macromolecule were synthesized. The group of polymers studied was obtained by free radical solution polymerization, using potassium persulfate as an initiator. The copolymerization of the monomers 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and acrylamide (AA) was carried out at different pH values of the reaction medium of the monomer mix. The copolymers were characterized by proton nuclear magnetic resonance spectroscopy (^1H NMR) and Fourier transform infrared spectroscopy (FTIR). The viscosity behavior of the co-

polymers in NaCl solution showed a dependency on the pH of the reaction medium, with higher pH leading to lower viscosities. The acidic conditions of this medium affect the initiator decomposition rate, which is a probable cause of the viscosity variation, and the extent of decomposition increases with increasing pH. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 192–198, 2003

Key words: copolymerization; acrylamide; 2-acrylamido-2-methylpropanesulfonic acid; synthesis; NMR; FTIR; spectroscopy; viscosity

INTRODUCTION

Several sulfonic acid copolymers have been studied by us to synthesize superabsorbent polymers because these substances have industrial application in pharmaceutical, agricultural, and other industries. Variation of the reaction solution pH leads to both non-hydrosoluble and hydrosoluble polymers, making it important to characterize the latter, as we do in the present study.

The monomers chosen for this study were 2-acrylamido-2-methylpropanosulfonic acid (AMPS) and acrylamide (AA). The molar ratio of the two monomers was optimized by the factorial design technique, and the best monomer molar ratio was 70:30, without corrections of the reaction solution pH. The influence of the pH on superabsorbency was subsequently observed; that is, at $\text{pH} \geq 5$, the copolymers synthesized became hydrosoluble. The solution properties of the copolymers were studied by viscometry, which is an important tool to characterize these copolymers.

The vinyl structure of the AMPS monomer (Figure 1) minimizes chain transfer reaction and permits high molecular weight generation compared with other sulfonic acid monomers. The AMPS monomer is known for its hydrolytic stability and a high tolerance

towards divalent cations,¹ thereby maintaining its capacity for propagation. The hydrolytic stability is due to the shielding effect produced by the unique geminal dimethyl structure of the monomer. Moreover, AMPS copolymers are widely utilized in several applications; such as, to precipitate solids in water clarification, as lubricants in personal care, in textile manufacture, and in oil fields.^{2,3}

The other monomer selected was acrylamide (AA). In short, the aforementioned features of the AMPS monomer and the availability and relative cheapness of the AA monomer led us to combine the advantages of these monomers, with which the polymerization of AA–AMPS was performed.

The objective of the research underlying the present study was to prepare and characterize water-soluble copolymers at different pHs of the monomers solution and to assess the effects of the pH on the copolymer structure and on the properties of its dilute solution.

The polyelectrolytes in the cited category of sulfonic acids can be produced by a variety of techniques; such as, solution polymerization, suspension polymerization, and inverse suspension polymerization. A practical method for the polymerization reaction for this purpose is solution polymerization. The low solubility of the monomer AMPS in organic solvents (e.g., 10 g/100 g ethanol, at 78°C) and its good solubility in water (~150 g/100 g water, at 25°C) indicate water as the preferred solvent for the preparation of the copolymers.

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EXPERIMENTAL

The synthesis of the copolymers reported was carried out by radical solution polymerization. The techniques of Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^1H NMR) spectroscopy were used as tools for the identification of functional groups and the confirmation of the structure of the copolymers obtained. Viscosity was measured in several aqueous sodium chloride solutions under standard conditions.

Synthesis of poly(AA-co-AMPS)

The monomers used in this study were acrylamide (AA) and 2-acrylamido-2-methyl-propanosulfonic acid (AMPS) supplied by Resiquímica, SA (Sintra, Portugal) and Lubrizol Corporation (Wickliffe, OH), respectively.

Polymerization was carried in a reactor equipped with a stirrer, a reflux condenser, a thermometer, a dropping funnel, and a gas inlet tube.

The monomers AA [itself a 50% (w/w) solution] and AMPS, in a molar ratio of 70:30, were dissolved in water. The ratio was optimized by a series of pre-screening runs. The pH value of the monomer solution was adjusted by the addition of aqueous sodium hydroxide (from Fisher Chemicals).

While stirring, U-type nitrogen was bubbled into the monomer solution for 3 h and the solution was heated to 50°C , after which aqueous potassium persulfate (from Merck) as an initiator was added in a dropwise manner into the monomer solution. This solution was polymerized at 50°C for 5 h. Under these circumstances, the reaction mixture becomes a clear viscous solution. After cooling to room temperature the copolymer was isolated by precipitation of the product by mixing the solution with acetone. Finally, the copolymer was dried in an oven at 60°C . After drying was completed, the copolymer was ground in a mortar to a fine powder, with a Sauter mean diameter of $\sim 20\ \mu\text{m}$.

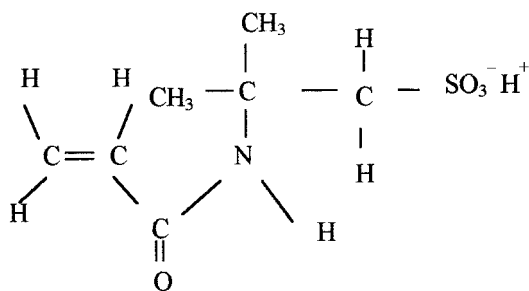


Figure 1 Structure of the AMPS monomer.

RESULTS AND DISCUSSION

Spectroscopic characterization

The structures of the synthesized copolymers were characterized by two spectroscopic techniques, FTIR and ^1H NMR spectroscopy. The FTIR spectrum was mainly used to determine whether two polymer samples are similar, by the identification of functional groups present in the molecule. These groups, as is known, give rise to characteristic absorption bands leading to identification.

The ^1H NMR spectroscopy results give information on which groups are present in the molecule as well as the quantitative relationship in which they are grouped.

Although the polymeric product is certainly a mixture containing some amount of the homopolymers poly(AA) and poly(AMPS), separation is not worth attempting, and the option was to observe the result of the reaction. Identification by fractionation of samples would not have the same effectiveness on the different samples and could somewhat distort the results, so fractionation was not used.

Fourier transform infrared spectroscopy (FTIR)

It was necessary to know whether the variation of the pH values of the monomeric solution would produce chemical changes in the structure of the polymeric molecule. With this objective, FTIR spectra of the materials seemed appropriate and measurements were made on the two monomers as well as on one of the copolymers. The superposition of spectra, each relating to one of two different pH values, was also made (Figure 5), the spectra showing similar patterns.

The FTIR absorbance spectra of the copolymers were obtained with a Perkin-Elmer Fourier transform infrared spectrophotometer (model 1600). The method involves mixing a fine powder of the sample with a matrix material, in this case potassium bromide (KBr), and pressing the mixture into a thin and compact transparent disc.

The transmission IR spectra of the monomers and copolymer AA-co-AMPS are shown in Figure 2, Figure 3, and Figure 4, respectively (most AA bands being contained in AMPS). The FTIR spectrum of AA (Figure 2) was characterized by the presence of the following vibration frequencies: $1672\ \text{cm}^{-1}$, typical of the C=O stretch; $3352/3182\ \text{cm}^{-1}$, NH_2 two/stretch; $1610\ \text{cm}^{-1}$, NH_2 deformation; and $1426\ \text{cm}^{-1}$ (generally not well resolved at $\sim 1400\ \text{cm}^{-1}$), characteristic of primary amides.

In the FTIR spectrum for AMPS (Figure 3), in addition to the typical NH_2 and C=O bands for AA, we found the sulfonic acid (SO_2) asymmetric, $1244\ \text{cm}^{-1}$, and symmetric, $1078\ \text{cm}^{-1}$, bands, both referred by Rao⁴ and others, who report 1250–1150 and 1100–1000

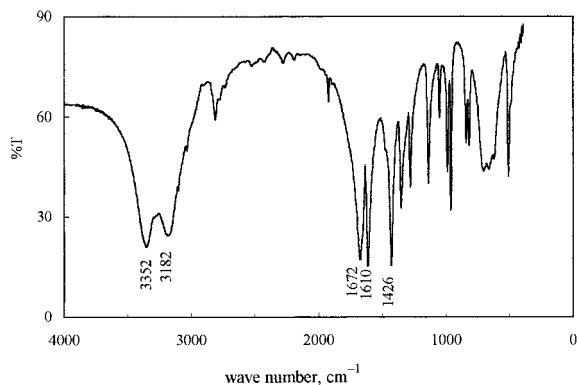


Figure 2 IR spectrum of the AA monomer.

cm^{-1} , respectively. The OH stretch band for the sulfonic acid corresponds to $\sim 3000 \text{ cm}^{-1}$.

The IR spectra of the copolymer synthesized at pH 7 is shown in Figure 4. In the spectrum of this copolymer, the following bands are observed: the two characteristic bands of NH_2 , at 3354 and 3208 cm^{-1} ; the deformation band of NH_2 , at 1544 cm^{-1} ; the stretching band of $\text{C}=\text{O}$, at 1676 cm^{-1} ; and the asymmetric and symmetric bands of SO_2 , at 1194 and 1042 cm^{-1} . The band corresponding to the OH bond in sulfonic acid is found at 2946 cm^{-1} .

By comparing the spectra of the copolymers synthesized at pH 7 and pH 9, it is observed that the characteristic frequencies are in the same region of the spectrum, showing no significant difference; that is, the chemical structure of the copolymers is therefore very similar.

It should be stressed that the effectiveness of the reaction between the monomers can be confirmed because the $\text{C}=\text{C}$ frequency of 980 cm^{-1} — characteristic of the vinyl monomers — has disappeared.

^1H nuclear magnetic resonance spectroscopy

For the structural determination of organic molecules, one of the most versatile techniques is NMR⁵ because it shows which groups exist and how they are com-

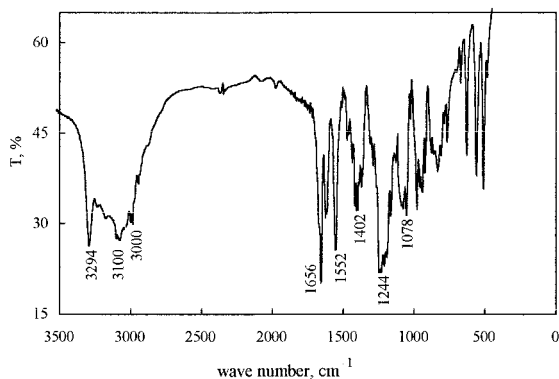


Figure 3 IR spectrum of the AMPS monomer.

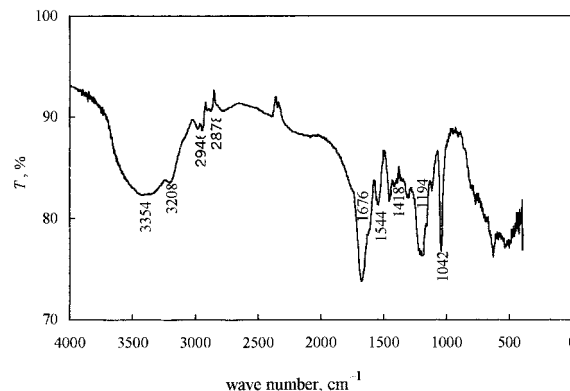


Figure 4 IR spectrum of the AA/AMPS copolymer produced at pH 7.

binated, as well as the number of protons in each group, in the case of ^1H NMR.

The copolymer poly(AA-co-AMPS) produced was analyzed by ^1H NMR. To determine the copolymer spectrum, a sample of it in the solvent chosen (deuterated water) was placed in a thin tube in the sample compartment (i.e., in the “probe”) of the NMR spectrometer, with an electromagnet at 300 MHz , for hydrogen resonance.

The pulse mode Fourier transform spectrum, in Figure 6, registers a series of peaks, although with a low resolution, in which the $\lambda 0.00$ peak corresponds to the internal reference tetramethylsilane (TMS). The low resolution has been assigned to the insufficient transparency of the copolymer sample, because of the dissolution time, which would lead to transparency. If that time is provided, the spectrum obtained has a higher resolution, shown in Figure 7, although the peak of the reference disappears. As known, the TMS is a very volatile compound (boiling point, 27°C) and evaporates during the absorption of the solvent, making the 0 Hz peak disappear after some time. Anyway,

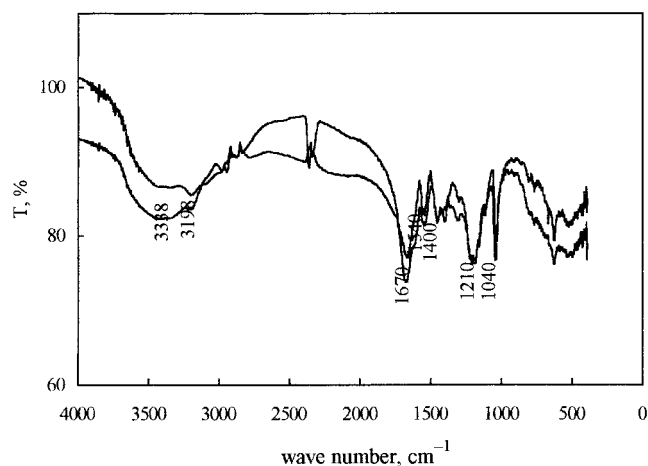


Figure 5 IR spectra of two AA/AMPS copolymers, synthesized at two pH values (pH 7 and pH 9).

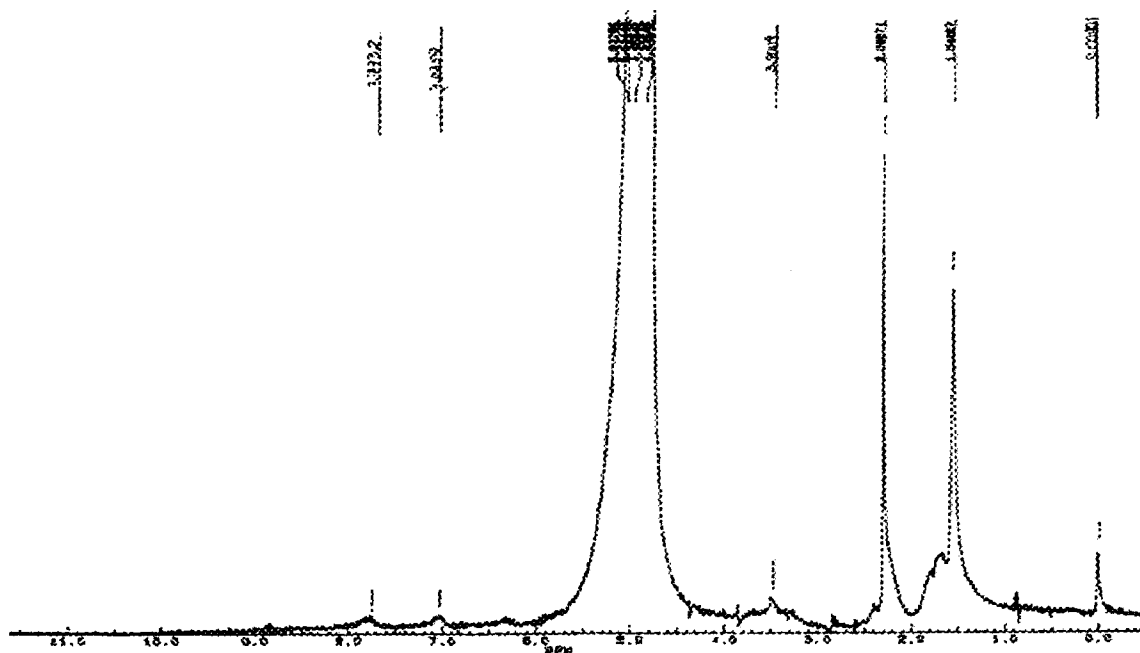


Figure 6 RMN spectrum of the copolymer AA/AMPS with TMS identification.

for the NMR scale, a 0 Hz peak was considered. This was made possible through a blank which was lead with deuterated water (D_2O) and TMS, providing a correct superposition, in Figure 7, through which the $\lambda 0$ can be confirmed.

It is known that $\lambda 0$ corresponds to the internal reference (TMS) and that the 4.62 ppm peak corresponds to the water in the solvent D_2O (D_2O/H_2O) and in the copolymer. So it is now possible to identify the absorp-

tion produced by the hydrogen atoms in each group, in accordance to the copolymer structure (Figure 8).

The peak with chemical deviation of 1.55 ppm corresponds to the hydrogens in the main chain; the hydrogen atoms of the CH_3 groups are detected at 2.30 ppm; the hydrogens of the CH_2 group bonded to SO_3H , at 3.5 ppm; and the peaks at 7.0 and 7.8 ppm correspond to the hydrogens of the NH and NH_2 groups, respectively. The peak for the proton of the

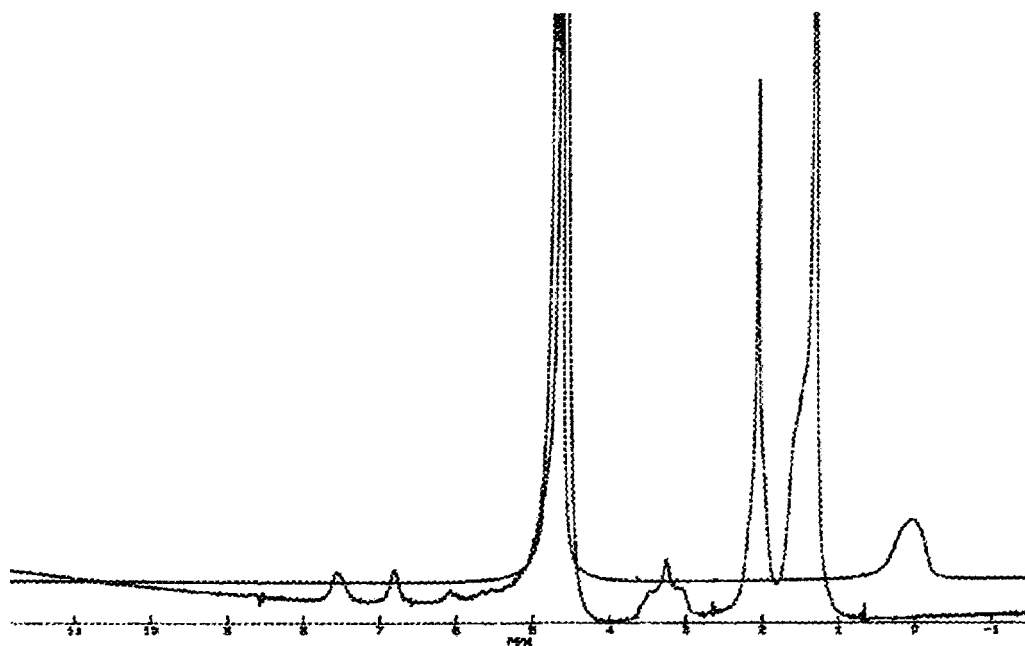


Figure 7 RMN spectrum of the copolymer AA/AMPS (no TMS identification).

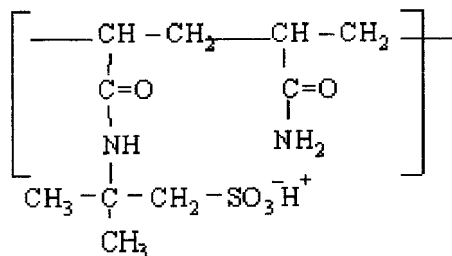


Figure 8 Structural segment of the copolymer AMPS/AA.

SO₃H group is not detected in the spectrum, indicating that this hydrogen is in permutation with the D₂O one and the one of water in the copolymer.

To obtain a quantitative analysis, the hydrogen count was made from peak integration, through the usual proportionality rules, as illustrated in Figure 9.

According to the relation of poly(Amps-co-AA) utilized for this copolymer (30:70) and its structure (Figure 8), it can be seen that AMPS presents two CH₃ groups equivalent to 6 H. Because the quantity of AMPS was 30%, then, theoretically, it would correspond to 180 H. From peak integration, in Figure 9, 138 H are calculated, leading to a real percentage of AMPS in the copolymer of 23%.

To confirm the existence of different structures of the copolymers poly(AA-co-AMPS) when produced at different pH, the ¹H NMR spectrum was determined for these copolymers for the low and high pH values, respectively, as shown in Figure 10. These spectra present similar peak deviations, only their intensity being different.

Viscosity measurements in NaCl solution

Viscosity measurements were selected because viscosity is proportional to molecular weight, namely in the spirit of the Mark-Houwink equation. The intrinsic viscosity was obtained by extrapolation of the reduced viscosity, η_{sp} / c , to infinite dilution.⁶ The dimensionless specific viscosity is determined as follows:

$$\eta_{sp} = (t - t_0) / t_0,$$

where t is the flow time for the solvent and t_0 is the flow time for the solution, both of which are proportional to the viscosities; and c is the polymer concentration. To eliminate the repulsive effect, which is inherent to the anionic polymer, the intrinsic viscosity was measured in aqueous NaCl solutions, as also reported by other researchers.⁷ The NaCl concentration sufficiently high for the polymer to present a neutral polymer behavior was determined to be 0.5 M.

The polymer solution was prepared by dissolving a known quantity of poly(AA-co-AMPS) in a 0.5 M NaCl solution (as already mentioned) at room temperature using a magnetic stirrer for agitation, which was carried until complete dissolution. Several dilutions of these base polymer solutions were subsequently prepared.

The viscosity experiments were performed at 25°C in an Ubbelohde-type viscometer, which enables flow time measurements. The temperature control of the viscometric bath was maintained to within 0.05°C by the use of a water bath equipped with a heater-circulator.

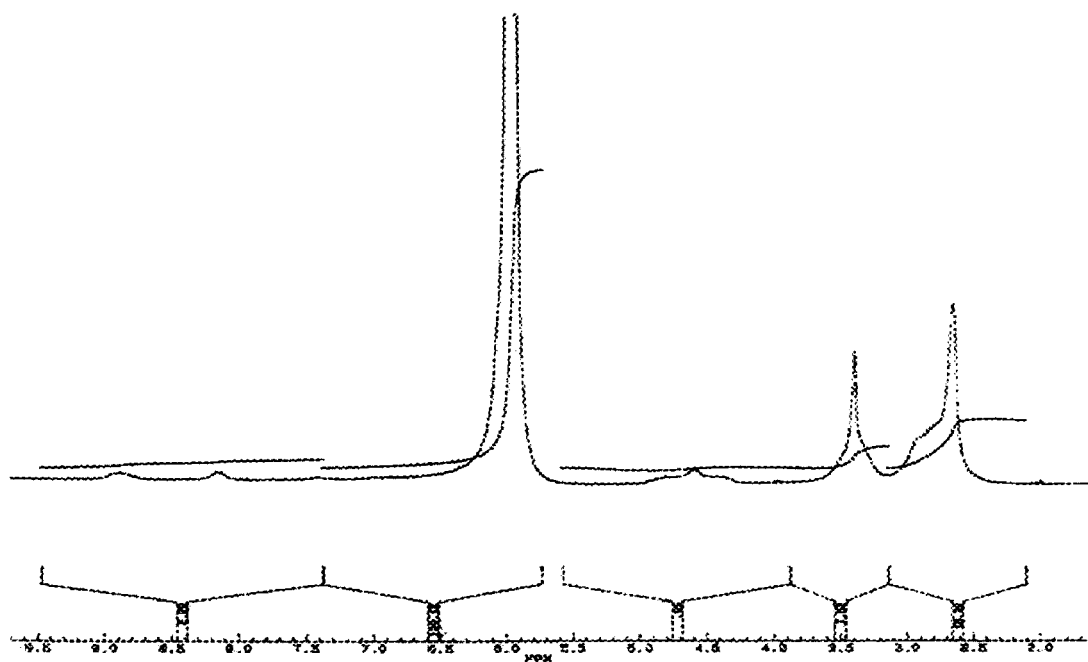


Figure 9 ¹H NMR spectrum of the copolymer AA/AMPS with area identification.

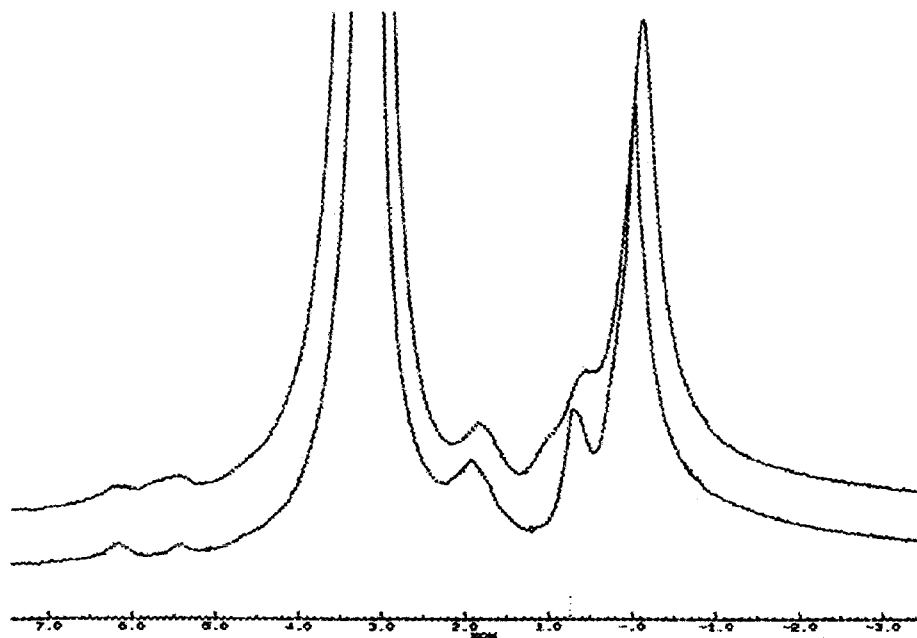


Figure 10 ^1H NMR spectrum of the copolymer AA/AMPS at two different pH values.

The dilute solution viscosity data of six samples obtained from copolymerization experiments are summarized in Table I. The data include the Huggins k' constant for each polymer obtained from the slope of the reduced viscosity curve, given by $\frac{\eta_{sp}}{c} = \eta + k'\eta^2c$.

A plot of the reduced viscosity versus concentration is shown in Figure 11 for the polymers synthesized. The plot in Figure 11 shows good linearity for all the lines, with a correlation coefficient of at least 0.9. The values observed for the Huggins constants for the samples of the polymers are in the vicinity of the 0.35 value⁸ normally seen for "flexible" polymers in a good solvent. The overlap parameter C^* , defined as the intrinsic viscosity multiplied by the concentration of the polymer solution, was obtained from the most concentrated solution. It is normally <1.0 for dilute solutions and between 1 and 10 for semidilute solutions. For the higher concentrations of poly(AA-co-AMPS) polymer solutions (i.e., >2 g/L), the NaCl solvent has a behavior that deviates from the dilute range. For the higher concentrations, the solution concentration appears to be in the semidilute range.

The influence of the reaction solution pH on viscosity appears to be negligible, although a certain decrease after pH 8 may be observed, as evident in the data in Table II and that plotted in Figure 12. In the vicinity of pH 7, nevertheless, the viscosity presents a slight peak, possibly due to equilibrium of the ionic charges.^{9, 10} The values of viscosity shown for each pH are the mean of three determinations, and the error mentioned in the figure was obtained as the difference between their extremes. The asterisk indicates experimental data variability.

Also, the potassium persulfate initiator used in the synthesis of the polymers is affected by the pH of the reaction medium, and the decomposition extent of the initiator increases with increasing pH.¹¹ The polymers synthesized presented a somewhat lower viscosity in the upper pH range.

The viscosity results of this study confirm the cited tendency regarding pH variation.

CONCLUSIONS

A class of hydrosoluble copolymers [poly(AA-co-AMPS)] were prepared in aqueous solution by radical

TABLE I
Intrinsic Viscosity and Huggins Constant from Copolymers AA-co-AMPS (70 : 30 ratio) at Different pH Values

Copolymer AA-co-AMPS	P-1	P-2	P-3	P-4	P-5	P-6
pH	5	6	7	8	9	10
Intrinsic viscosity, η'	679	648	737	689	512	387
Huggins constant, k'	0.43	0.52	0.54	0.58	0.46	0.38
Correlation coefficient	0.996	0.989	0.995	0.998	0.997	0.981
Overlap parameter, C^*	1.70	1.62	1.84	1.72	1.28	0.97

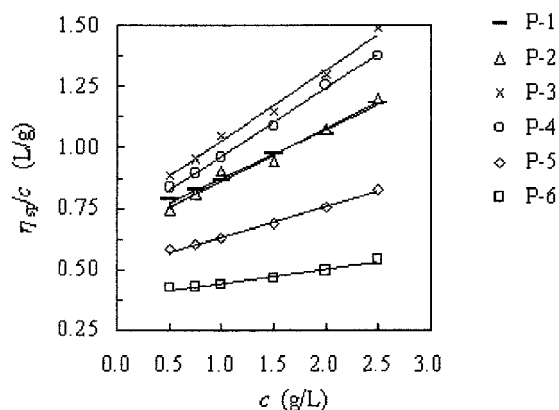


Figure 11 Reduced viscosity *vs.* concentration of copolymer solutions, in 0.5 M NaCl solution.

polymerization of the monomer acrylamide (AA) with a monomer of sulfonic acid (AMPS) at various pH values, using potassium persulfate as the polymerization initiator. The structural characterization of the polymers was accomplished by FTIR and ^1H NMR spectroscopy, and the expected bands and groups were confirmed. The determination of viscosity in NaCl solution at 25°C led to values that show a dependency on the pH of the reaction medium: in accordance with previous research, a higher pH yielding lower viscosities. A probable explanation for the variability in the viscosity values is the effect of the acidic

TABLE II
Intrinsic Viscosity versus pH in the Reaction Solution

Copolymer	P 1	P 2	P 3	P 4	P 5	P 6
pH	5	6	7	8	9	10
η	679	648	737	689	512	387
Error ^a	17%	9%	15%	14%	7%	8%

^a Experimental data variability.

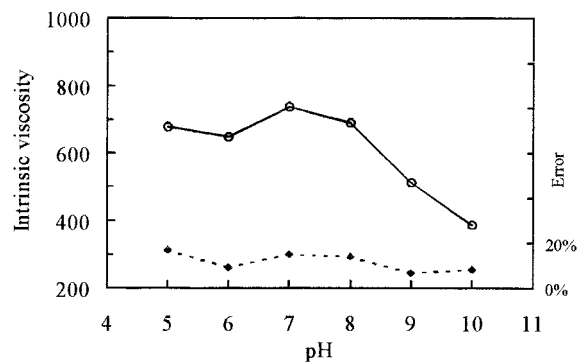


Figure 12 Intrinsic viscosity *vs.* pH of reaction medium.

conditions on the initiator decomposition rate. Indeed, the decomposition extent of the initiator (potassium persulfate) increases with increasing pH. The results obtained confirm this previous observation.

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