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# Synthesis, Characterization, and Potentiometric Behavior of Cationic Polyelectrolytes

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# SYNTHESIS, CHARACTERIZATION, AND POTENTIOMETRIC BEHAVIOR OF CATIONIC POLYELECTROLYTES

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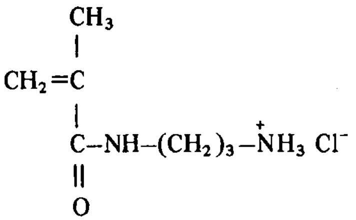
## ABSTRACT

Various amino monomers differing in the number of amine groups and the environment of the site were synthetized. These monomers were copolymerized with acrylamide, and the polymeric ammonium salts were characterized by viscometry, light scattering, and pH titration. Evidence of interactions between neighboring cationic sites was observed for a copolymer with a high local charge density due to three amino groups in the comonomer unit.

## INTRODUCTION

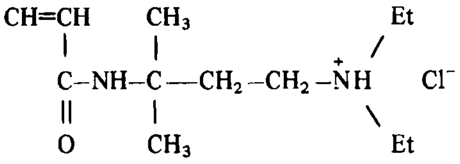
Polymeric amines and ammonium salts have attracted the attention of both industrial and academic researchers in recent years. They behave as polymeric base and have found applications as reagents for organic supported synthesis, as complexing agent, and in the purification of wastewaters, flocculation, etc. [1-3].

In this work we synthetized several cationic polyelectrolytes by copolymerization of acrylamide with a basic monomer. The following three different vinylic ammonium salts were prepared:

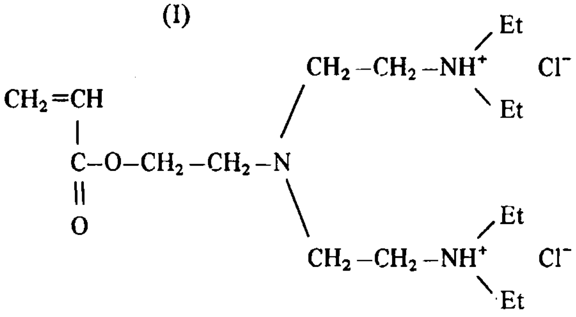


$$CH_2{=}C(CH_3){-}C(=O){-}NH{-}(CH_2)_3{-}\overset{+}{N}H_3\ Cl^-$$

(I)



(II)



(III)

and a series of copolymers was obtained with variable charge density and with various hydrophobic groups. Neighbor functional group interactions are obtained from potentiometric titration data.

## EXPERIMENTAL

$^1H$ NMR spectra at 90 MHz were run on a Varian EM 90 instrument. The $^1H$ NMR analysis of the amine mixture obtained during Monomer II synthesis was performed on a 250-MHz (Bruker WP) spectrometer. $^{13}C$ NMR spectra were taken on a Varian FT 80 or on a 250-MHz (Bruker WP) instrument. Mass spectra were measured on a Perkin-Elmer RMU-6E spectrometer.

Elemental analysis were carried out by the Microanalytical Laboratory, CNRS, Lyon.

Intrinsic viscosities were determined at 30°C with a Fica Automatic capillary viscometer by a double extrapolation to zero concentration:

$$[\eta] = \lim_{C\to 0} \frac{t - t_0}{t_0 C} = \lim_{C\to 0} \frac{1}{C} \ln \frac{t}{t_0}, \tag{1}$$

where $t$ represents the flow time of the solution and $t_0$ is the flow time of the solvent. The polymers were dissolved in 1 $M$ aqueous NaCl.

Light-scattering measurements were performed on a modified Fica 42000 instrument equipped with a He-Ne Laser. Polarized light of 6 328 Å wavelength was used. The concentration of the stock solution was 1-2 g/L of polymer in 1 $M$ NaCl. Dust was carefully removed from the solutions by centrifugation for 2 h at 20 000 *g*. A Brice-Phoenix differential refractometer, calibrated with saccharose solutions, was used to measure the refractive index increment, *dn/dc*, at 632.8 nm.

Titrations were carried out with a Tacussel Model Titrimat instrument. The content of cationic sites in the copolymers was determined by titration of $Cl^-$ with $AgNO_3$ using a Tacussel unitubular $Ag\text{-}Hg/Hg_2SO_4$ electrode. pH was determined with a pH meter fitted with a glass electrode (Tacussel Model TBC 11/HA).

Acid-base titrations were carried in a thermostated cell at 25°C. The glass electrode was calibrated with two buffers, pH = 3 and pH = 9. Monomers and copolymers, initially in the ionic form (i.e., $-N^+-Cl^-$), were neutralized with an excess of NaOH and backtitrated with HCl. Monomer and polymer concentrations were 5-10 meq/L.

## MONOMER SYNTHESES

### (Methacrylamidopropyl)ammonium Chloride (I)

This monomer was prepared according to the literature [4]. The crude product was purified by successive recrystallizations from isopropanol, yield 30%. $(C/N)_{calc} = 3$, $(C/N)_{found} = 3.05$, $(C/Cl)_{calc} = 2.36$, $(C/Cl)_{found} = 2.3$. $^1$H NMR: solvent $D_2O$; reference DSS; 5-6(*m*, 2H, $\underline{CH}_2{=}\overset{|}{C}{-}$), 3.4(*t*, 4H, $-\underset{\underset{O}{\|}}{C}-NH-\underset{a}{\underline{CH}_2}-C-\underset{b}{\underline{CH}_2}-\overset{+}{N}\leq$), 2(*m*, 5H, $C{=}\underset{\underset{\underline{CH}_3}{|}}{C}-CONH$ and $HN-CH_2-\underline{CH}_2-CH_2$). $^{13}$C NMR: solvent $D_2O$; reference $CH_3CN$; 171.2($-\underset{|}{C}{=}O$), 120.05 and 137.9($\underline{CH}_2{=}\underline{\overset{|}{C}}{-}$), 36.2 and 35.3($HN-\underline{CH}_2-C$ and $\dot{N}-\underline{CH}_2-C$), 25.8($C-\underline{CH}_2-C$), 16.8($C{=}\underset{\underset{\underline{CH}_3}{|}}{C}$).

### (1,1-Dimethyl-3-diethylaminopropyl)acrylamide (II)

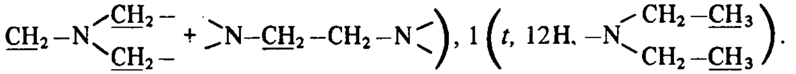
Monomer II was prepared according to the literature [5]. $(C/N)_{calc} = 5.1$, $(C/N)_{found} = 5$, $(C/Cl)_{calc} = 4.06$, $(C/Cl)_{found} = 4.05$. $^{1}N$ NMR: solvent $D_2O$; reference DSS; 5.6-6.4(*m*, 3H, $\underline{CH_2}=\underline{CH}$), 3.2(*q*(b), *t*(a), 6H, $\underset{(a)}{CH_2}-CH_2-\overset{+}{N}\begin{array}{l}CH_2-CH_3\\ CH_2-CH_3\\ (b)\end{array}$, 2.2(*t*, 2H, $-\overset{|}{\underset{|}{C}}-\underline{CH_2}$), 1.4 $\left(s, 6H, -\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\right)$, 1.3 $\left(t,(c), 6H, -\overset{+}{N}H\begin{array}{l}CH_2-CH_3\ (c)\\ CH_2-CH_3\ (c)\end{array}\right)$. $^{13}C$ NMR: solvent $D_2O$; reference $CH_3CN$; 167($-\overset{|}{C}=O$), 129.8-126.1($\underline{CH_2}=\underline{CH}$), 51.6 $\left(-\overset{|}{\underset{|}{N}}-\underline{C}\right)$, 46.76 and 46.6$\left(-\overset{+}{N}H\begin{array}{l}\underline{CH_2}-\\ \underline{CH_2}-\end{array}\right)$, 30.9$\left(-\overset{|}{\underset{|}{C}}-\underline{CH_2}\right)$, 25.45$\left(-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-\right)$, 7.4$\left(\overset{+}{N}H\begin{array}{l}C-CH_3\\ C-CH_3\end{array}\right)$.

### Bis(diethylaminoethyl)aminoethanol (IV)

This intermediate was prepared according to the literature [6], yield 63%. $^{1}H$ NMR: solvent $CD_3OD$; reference TMS; 3.6(*t*, 2H, HO–$\underline{CH_2}$–$\underline{CH_2}$). 2.5 $\left(q + t, 18H, \underline{CH_2}-N\begin{array}{l}\underline{CH_2}\\ \underline{CH_2}\end{array} \text{and } HO-\underline{CH_2}-CH_2-N, N-\underline{CH_2}-CH_2-N\right)$, 1 $\left(t, 12H-N\begin{array}{l}CH_2-\underline{CH_3}\\ CH_2-\underline{CH_3}\end{array}\right)$. Mass spectrum (70 eV): 259$\left(M^+, HO-C-C-N\begin{array}{l}C-C-N(Et)_2\\ C-C-N(Et)_2\end{array}\right)$, 228$\left(C=\overset{+}{N}\begin{array}{l}C-C-N(Et)_2\\ C-C-N(Et)_2\end{array}\right)$, 173$\left(HO-C-C-N^{+}\begin{array}{l}=C-\\ C-C-N(Et)_2\end{array}\right)$, 86$\left(\text{base peak}, CH_2=N^{+}\begin{array}{l}Et\\ Et\end{array}\right)$.

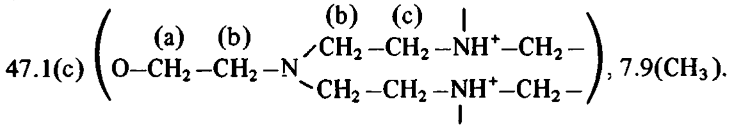
### Bis(diethylaminoethyl)aminoethyl Acrylate (III)

The reaction of acryloyl chloride with Compound IV, following the experimental procedure given in the literature [6, 7], leads to Monomer III, a colorless liquid, yield 60%. $^{1}H$ NMR: solvent $CDCl_3$; reference TMS; 6.5-5.5(*m*, 3H, $\underline{CH_2}=\underline{CH}$), 4.2 $\left(t, 2H, O-\underset{\underset{O}{\|}}{C}-\underline{CH_2}-CH_2-N\!<\right)$, 2.5$\left(q + t,\right.$ 18H,



$$\underline{CH}_2-N\begin{matrix}\diagup \underline{CH}_2- \\ \diagdown \underline{CH}_2-\end{matrix} + \rangle N-\underline{CH}_2-CH_2-N\langle\Bigg),\ 1\left(t,\ 12H,\ -N\begin{matrix}\diagup CH_2-\underline{CH}_3 \\ \diagdown CH_2-\underline{CH}_3\end{matrix}\right).$$

A dry dichlorhydrate compound is difficult to obtain, thus it was preferred to keep it in solution. The experimental procedure was as follows. To a 500-mL vial, 20 g monomer, 50 mL ethyl ether, and 400 mL water containing 2 equiv HCl were added. After vigorous stirring, the aqueous and organic phases were separated by decantation. The aqueous phase was concentrated under high vacuum to prevent acrylate hydrolysis. The concentration of the solution was determined by potentiometric titration. $^{13}C$ NMR: solvent $D_2O$; reference $CH_3CN$; 167(C=O), 132.2 and 126.1 ($CH_2{=}CH$), 59.8(a), 48.4(b),



$$47.1(c)\left(\overset{(a)}{O-CH_2}-\overset{(b)}{CH_2}-N\begin{matrix}\diagup \overset{(b)}{CH_2}-\overset{(c)}{CH_2}-\overset{|}{NH^+}-CH_2- \\ \diagdown CH_2-CH_2-\underset{|}{NH^+}-CH_2-\end{matrix}\right),\ 7.9(CH_3).$$

## ACRYLAMIDE COPOLYMER SYNTHESES

The cationic copolymers were prepared according to the following general procedure: 0.252 mol acrylamide and 0.028 mol Monomer I were introduced in 260 mL deionized water. Air was flushed from the reaction vessel by nitrogen for 30 min. Then 20.2 mg of $(NH_4)_2S_2O_8$ dissolved in 10 mL water was introduced in the reactor with vigorous stirring, followed by 12.3 mg sodium disulfite in 10 mL $H_2O$. The solution was kept at 60°C for 3 h. After cooling, the solution was poured in a large volume of acetone, and the precipitated polymer was finally dried under high vacuum and powdered.

Experimental conditions for the synthesis of the copolymers are given in Table 1. All copolymers were ultrafiltered with an Amicon apparatus through a membrane reported to give $10^5$ mass exclusion (Amicon). After ultrafiltration, the polymers were freeze dried. The cationic site content is shown in Table 2.

## RESULTS AND DISCUSSION

### Monomer Preparation and Polymerization

Monomer I was prepared in two steps. In the first step both amino groups of the propanediamine were neutralized with an excess of methacrylic acid.

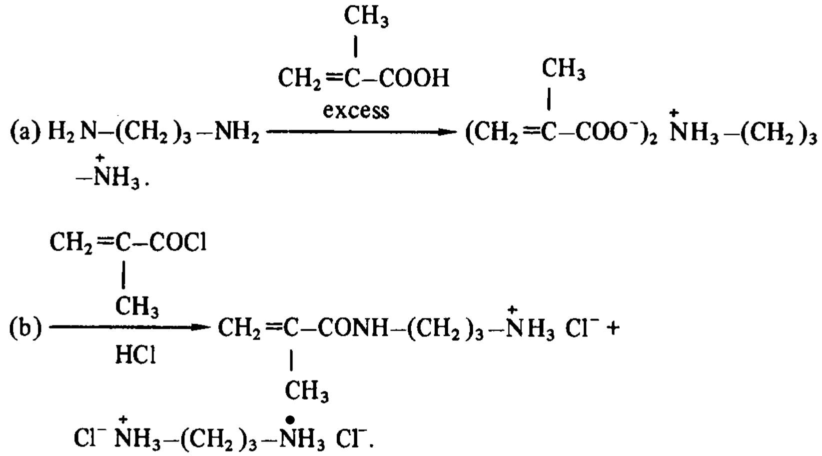
TABLE 1. Experimental Conditions for Copolymerization of Acrylamide with Various Cationic Monomers

| Copolymer | Copolymer of | % Cationic monomer | Monomer, mol/L | $(NH_4)_2S_2O_5$, mmol/L | $Na_2S_2O_5$, mmol/L | Temperature, °C, and time, h, of polymerization | Conversion, % |
|---|---|---|---|---|---|---|---|
| 1 | Acrylamide-(I) | 10 | 1 | 0.316 | 0.231 | 60, 3 | 95 |
| 2 | Acrylamide-(I) | 40 | 1 | 0.316 | 0.231 | 60, 3 | 93 |
| 3 | Acrylamide-(II) | 10 | 1 | 0.316 | 0.231 | 60, 3 | 91 |
| 4 | Acrylamide-(II) | 25 | 1 | 0.316 | 0.231 | 60, 3 | 95 |
| 5 | Acrylamide-(II) | 35 | 1 | 0.316 | 0.231 | 60, 3 | 90 |
| 6 | Acrylamide-(III) | 10 | 1 | 0.316 | 0.231 | 60, 3 | 85 |
| 7 | Acrylamide-(III) | 15 | 1 | 0.964 | 0.71 | 60, 3 | 95 |
| 8 | Acrylamide-(III) | 25 | 1 | 0.948 | 0.693 | 60, 3 | 95 |
| 9 | Acrylamide-(III) | 45 | 0.8 | 0.275 | 0.21 | 60, 3 | 90 |

TABLE 2. Copolymer Composition Determined by Microanalysis and Potentiometry

| No. | Water, % | Cl, meq/g | Cationic site (microanalysis), % | Cationic site (potentiometry), % |
|---|---|---|---|---|
| 1 | 15 | 1.06 | 10 | 10 |
| 2 | 10 | 2.76 | 32 | 32 |
| 3 | 8 | 0.62 | 6 | 6 |
| 4 | 10 | 1.76 | 21 | 21 |
| 5 | 10 | 1.84 | 25 | 23 |
| 6 | 10 | 0.54 | 5 | 5 |
| 7 | 10 | 0.85 | 10 | 10 |
| 8 | 15 | 1.18 | 20 | 18 |
| 9 | 17 | 1.5 | 28 | 27 |

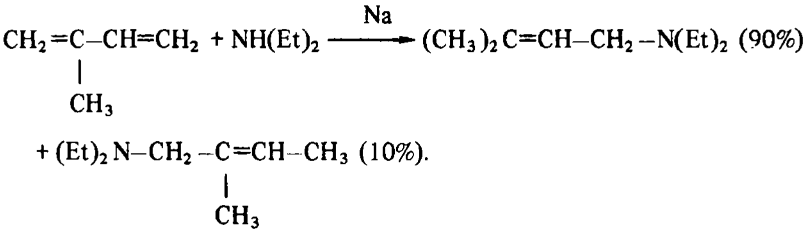
Then one of the amino group was deprotected by the stoichiometric addition of methacryloyl chloride to obtain the monoacrylate:



$$\text{(a) } H_2N\text{–}(CH_2)_3\text{–}NH_2 \xrightarrow[\text{excess}]{CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}\text{–}COOH} (CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}\text{–}COO^-)_2\ \overset{+}{N}H_3\text{–}(CH_2)_3\text{–}\overset{+}{N}H_3.$$

$$\text{(b) } \xrightarrow[HCl]{\underset{\underset{\displaystyle CH_3}{|}}{CH_2=C}\text{–}COCl} \underset{\underset{\displaystyle CH_3}{|}}{CH_2=C}\text{–}CONH\text{–}(CH_2)_3\text{–}\overset{+}{N}H_3\ Cl^- + Cl^-\ \overset{+}{N}H_3\text{–}(CH_2)_3\text{–}\overset{\bullet}{N}H_3\ Cl^-.$$

The synthesis of Monomer II is based on a three-step procedure. (a) Addition of diethylamine to isoprene:

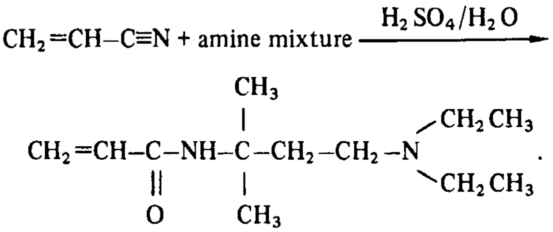


$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2 + NH(Et)_2 \xrightarrow{Na} (CH_3)_2C{=}CH{-}CH_2{-}N(Et)_2\ (90\%)$$

$$+ (Et)_2N{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_3\ (10\%).$$

The amine ratio was determined by $^1H$ NMR (Fig. 1).

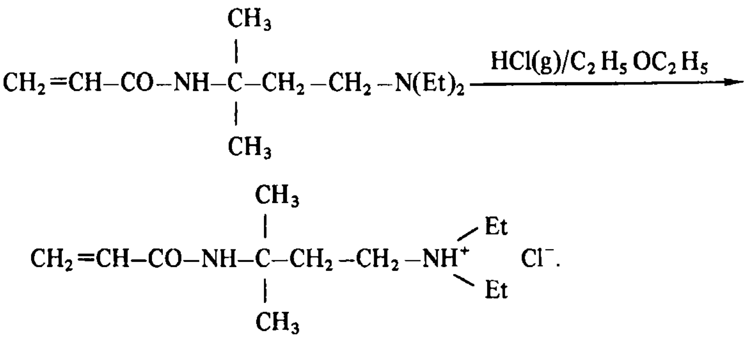
(b) Ritter reaction:



$$CH_2{=}CH{-}C{\equiv}N + \text{amine mixture} \xrightarrow{H_2SO_4/H_2O}$$

$$CH_2{=}CH{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2{-}CH_2{-}N\begin{matrix}\nearrow CH_2CH_3\\ \searrow CH_2CH_3\end{matrix}\ .$$

(c) Chlorhydrate formation:



$$CH_2{=}CH{-}CO{-}NH{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2{-}CH_2{-}N(Et)_2 \xrightarrow{HCl(g)/C_2H_5OC_2H_5}$$

$$CH_2{=}CH{-}CO{-}NH{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2{-}CH_2{-}NH^+\begin{matrix}\nearrow Et\\ \searrow Et\end{matrix}\quad Cl^-.$$

Monomer III was prepared according to a three-step scheme. (a) Amino alcohol synthesis:

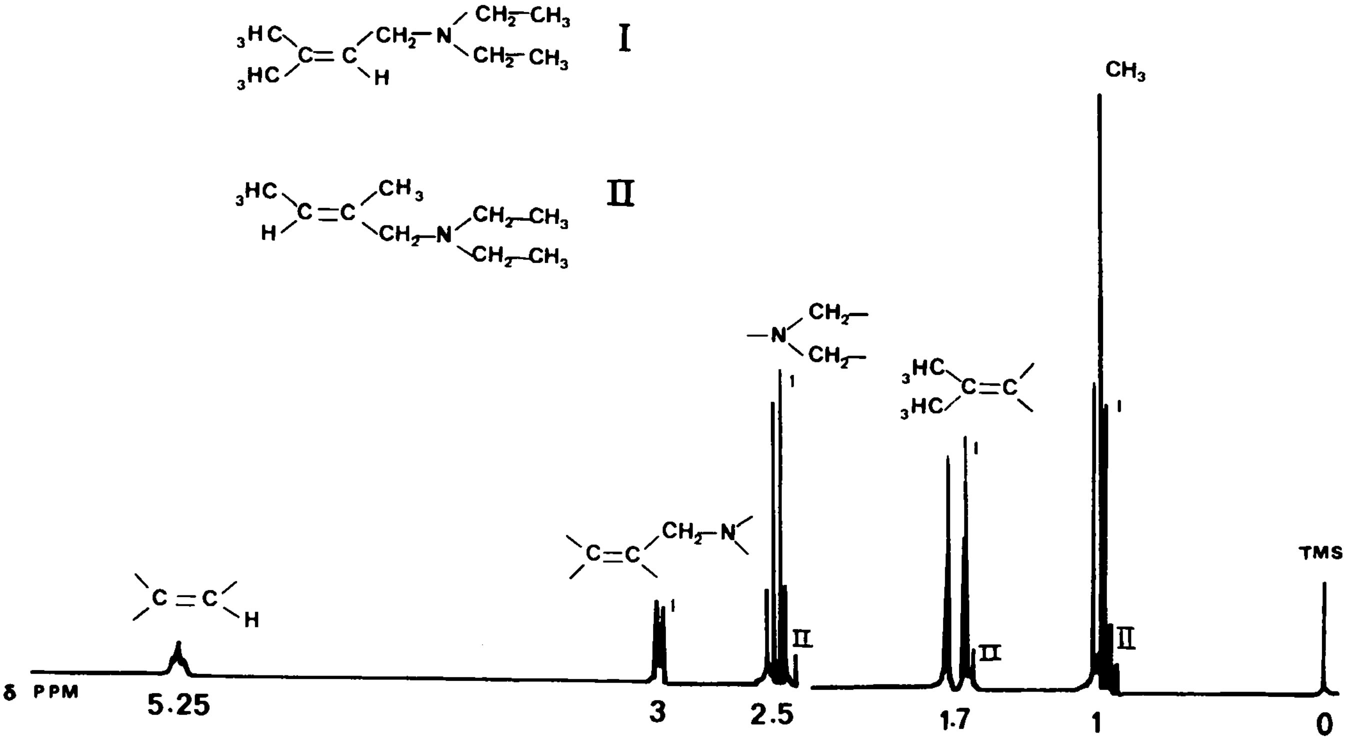
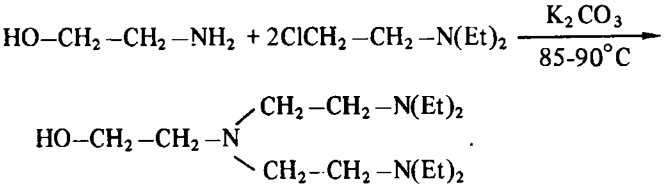
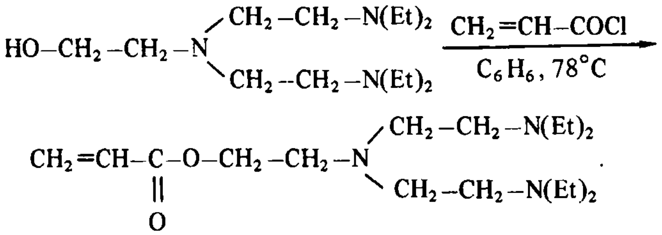


FIG. 1. Proton NMR of amine isomers.



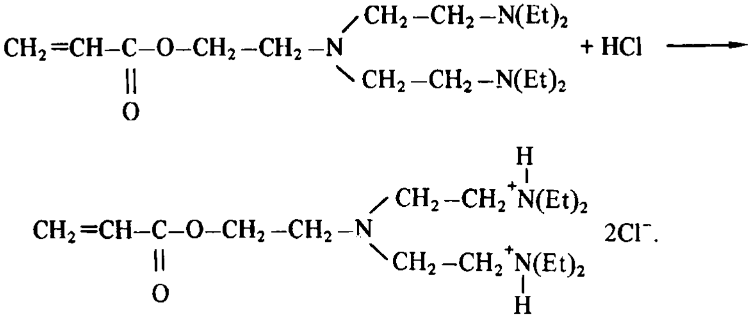
$$HO{-}CH_2{-}CH_2{-}NH_2 + 2ClCH_2{-}CH_2{-}N(Et)_2 \xrightarrow[85\text{-}90^\circ C]{K_2CO_3} HO{-}CH_2{-}CH_2{-}N\begin{array}{l} \diagup CH_2{-}CH_2{-}N(Et)_2 \\ \diagdown CH_2{-}CH_2{-}N(Et)_2 \end{array}.$$

(b) Acrylate derivative preparation:



$$HO{-}CH_2{-}CH_2{-}N\begin{array}{l} \diagup CH_2{-}CH_2{-}N(Et)_2 \\ \diagdown CH_2{-}CH_2{-}N(Et)_2 \end{array} \xrightarrow[C_6H_6,\ 78^\circ C]{CH_2{=}CH{-}COCl} CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}N\begin{array}{l} \diagup CH_2{-}CH_2{-}N(Et)_2 \\ \diagdown CH_2{-}CH_2{-}N(Et)_2 \end{array}.$$

(c) Dichlorhydrate formation:



$$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}N\begin{array}{l} \diagup CH_2{-}CH_2{-}N(Et)_2 \\ \diagdown CH_2{-}CH_2{-}N(Et)_2 \end{array} + HCl \longrightarrow CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}O{-}CH_2{-}CH_2{-}N\begin{array}{l} \diagup CH_2{-}CH_2{-}\overset{\overset{H}{|}}{\overset{+}{N}}(Et)_2 \\ \diagdown CH_2{-}CH_2{-}\underset{\underset{H}{|}}{\overset{+}{N}}(Et)_2 \end{array} 2Cl^-.$$

Various cationic copolymers having different structures and compositions were prepared by the radical copolymerization of Monomers I, II, and III with acrylamide. The copolymerizations were carried out in aqueous solution with ammonium peroxodisulfate-sodium disulfite as initiator.

The copolymers were characterized by viscometry and light scattering (Table 3). Figure 2 shows the viscometric behavior in 1 *M* NaCl for one of the samples, 4, as an example. In 1 *M* NaCl we observed a linear dependence of $\eta_{sp}/C_p$ on $C_p$. Extrapolation for $C_p = 0$ gives the intrinsic viscosity, $[\eta]$.

Zimm plots of light-scattering results for polyelectrolytes depend on the charge density of the macroion. To suppress this influence, experiments are generally performed in salt solution. Figure 3 shows the Zimm plot obtained for Copolymer 2 in 1 *M* NaCl.

TABLE 3. Viscometric and Light-Scattering Results

| Copolymer no. | Cationic site, % | $[\eta]^{30^\circ\mathrm{C}}$ in 1 $M$ NaCl, dL/g | $(dn/dc)_{634.1}$ in 1 $M$ NaCl | $\bar{M}_w \times 10^{-5}$ | $(\bar{R}_g{}^2)^{1/2}$, nm | $A_2 \times 10^4$, mL/g$^2$ |
|---|---|---|---|---|---|---|
| 1 | 10 | 1.7 | 0.169 | 6.5 | 44.8 | 4.17 |
| 2 | 32 | 0.98 | 0.172 | 4.9 | 41.6 | 2.0 |
| 3 | 6 | 3.43 | 0.170 | 7.3 | 91.0 | 3.8 |
| 4 | 21 | 1.45 | 0.175 | 4.2 | 38.3 | 4.2 |
| 5 | 23 | 2.07 | 0.178 | 10 | 72.2 | 3.1 |
| 6 | 5 | 2.69 | 0.172 | 25 | 108.1 | 1.44 |
| 7 | 10 | 2.5 | 0.172 | 23 | 126.6 | 2.44 |
| 8 | 18 | 1.33 | 0.172 | 9.6 | 56.4 | 3.8 |
| 9 | 27 | 0.82 | 0.174 | 7.1 | 51.4 | 2.3 |

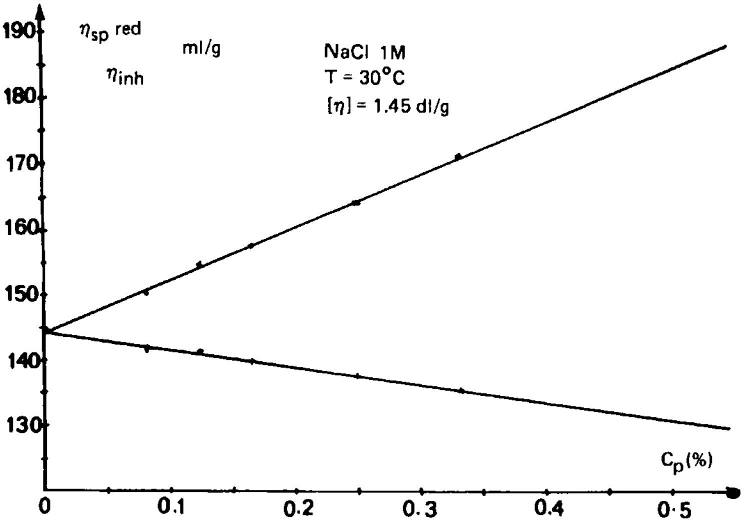


FIG. 2. Intrinsic viscosity determination of Copolymer 4 in 1 *M* NaCl.

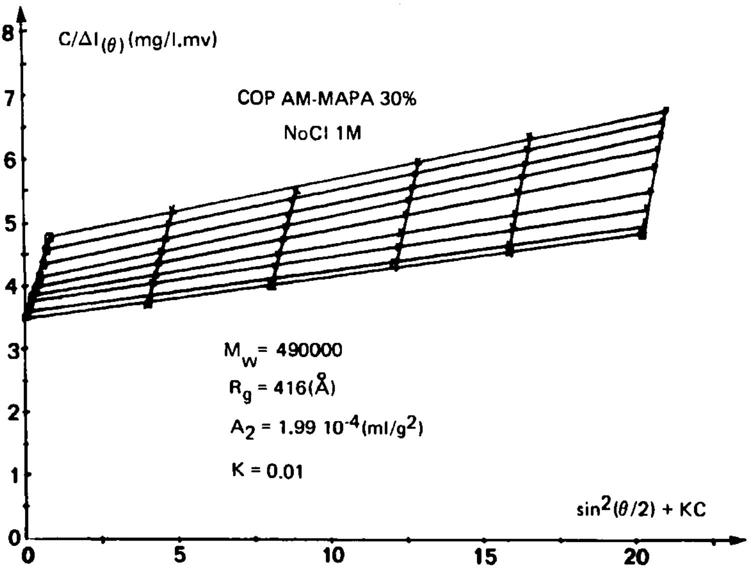


FIG. 3. Zimm plot for Copolymer 2 in 1 *M* NaCl.

The random copolymers prepared in this work had 5-30% of cationic site and a molar mass between about $5 \times 10^5$ and several millions.

## POTENTIOMETRIC BEHAVIOR

Experimental and theoretical treatments have shown that the ionization of the carboxylic sites of a polyacid (e.g., polyacrylic acid) depends strongly on the electrostatic potential of the chain [8-11]. Thus, for a polyelectrolyte, the relation between pH and $\alpha$ (degree of ionization) is given by

$$\mathrm{pH} = \mathrm{p}k_0 - \log \frac{1-\alpha}{\alpha} + (0.4343/kT)q\psi_0, \tag{2}$$

where $k_0$ is the intrinsic dissociation constant and $q\psi_0$ is the electrical work necessary to add a charge $q$ to the polyion.

When a base is added to a solution of a polyacid, the polymer charge density increases and the energy required for the ionization of an acid group also increases. Consequently, the dissociation constant depends on the degree of ionization and the charge of the macroion. To determine the apparent dissociation constant, several empirical equations have been proposed [12-14]. In this work we have used the relation given by Katchalsky and Spitnik [14]:

$$\mathrm{pH} = \mathrm{p}k_a - n \log \frac{1-\alpha}{\alpha}. \tag{3}$$

For a polyelectrolyte, the parameter $n$ differs from unity and measures the "polyelectrolyte effect."

Among the monomeric amines and ammonium salts prepared in this work, we expected the most appreciable "polyelectrolyte effect" with the acrylamide-triamine (III) copolymers because of the high charge density of their functional group. Thus our study was focused on the potentiometric behavior of Monomer III and its copolymers.

### Titration of Monomer (III) and Its Copolymers

The following three equations are involved when the triamine is dissolved in aqueous solution:

$$LH_3{}^{3+} \rightleftharpoons H^+ + LH_2{}^+, \quad k_1 = [H^+][LH_2{}^{2+}]/[LH_3{}^{3+}], \tag{4}$$

$$LH_2{}^{2+} \rightleftharpoons H^+ + LH^+, \quad k_2 = [H^+][LH^+]/[LH_2{}^{2+}], \tag{5}$$

$$LH^+ \rightleftharpoons H^+ + L, \quad k_3 = [H^+][L]/[LH^+]. \tag{6}$$

The three successive dissociation constants $k_1$, $k_2$, and $k_3$ can be determined from the titration curve. The required values are obtained using the protonation function $\bar{n}_H$ [4] following the calculation of Yperman and coworkers [15]:

$$\bar{n}_H = [H^+]_{\text{bound}}/C_L, \tag{7}$$

where $C_L$ represents the total concentration of the ligand according to

$$C_L = [L] + [LH^+] + [LH_2]^{2+} + [LH_3{}^{3+}] \tag{8}$$

and

$$[H^+]_{\text{bound}} = [HL] + 2[LH_2{}^{2+}] + 3[LH_3{}^{3+}], \tag{9}$$

leading to

$$\bar{n}_H = \frac{[LH] + 2[LH_2{}^{2+}] + 3[LH_3{}^{3+}]}{[L] + [LH] + [LH_2{}^{2+}] + [LH_3{}^{3+}]} \tag{10}$$

On introducing the overall formation constants,

$$\beta_{11} = \frac{[HL^+]}{[H^+][L]}, \quad \beta_{12} = \frac{[HL^{3+}]}{[H^+]^2[L]}, \quad \beta_{13} = \frac{[HL^{3+}]}{[H^+]^3[L]}, \tag{11}$$

Equation (10) becomes

$$\bar{n}_H \frac{\beta_{11}[H^+] + 2\beta_{12}[H^+]^2 + 3\beta_{13}[H^+]^3}{1 + \beta_{11}[H^+] + \beta_{12}[H^+]^2 + \beta_{13}[H^+]^3} \tag{12}$$

The values of $\bar{n}_H$ can be determined experimentally from the titration curve of Monomer III with HCl:

$$\bar{n}_H = \frac{C_A - H^+ + [OH^-]}{C_L}, \tag{13}$$

where $C_A$ represents the acid concentration. Finally, a modification of Eq. (12) gives the expression

$$\beta_{11}(\bar{n}_H - 1)[H^+] + \beta_{12}(\bar{n}_H - 2)[H^+]^2 + \beta_{13}(\bar{n}_H - 3)[H^+]^3 = -\bar{n}_H, \tag{14}$$

which can be solved for the formation constants from three data points, i.e., three $\bar{n}_H$ values.

The dissociation constants thus calculated from the titration curve (Fig. 4) are shown in Table 4.

Only small differences are observed between copolymers having different contents of cationic sites, but a plot of pH versus log $[\alpha/(1 - \alpha)]$ gives a straight line with a slope of 1.4 (Fig. 5). The fact that the slope differs from one is evi-

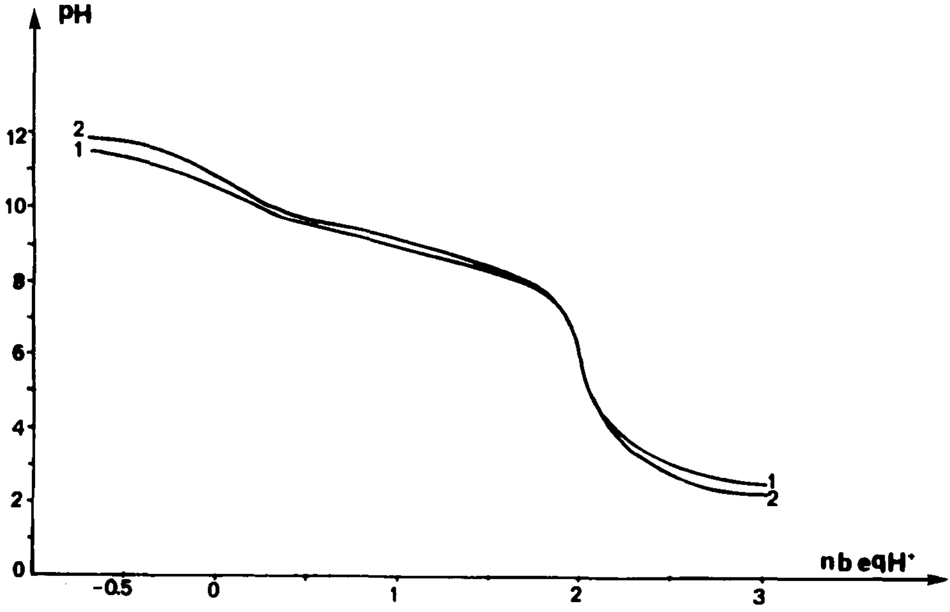


FIG. 4. Titration curves for Monomer (III). $C$ = 6 mmol/L (Curve 1) and for Copolymer 9, $C_p$ = 10 meq/L (Curve 2).

TABLE 4. Dissociation Constants Obtained from Titration Curves

| | p$k_3$ | p$k_2$ | p$k_1$ |
|---|---|---|---|
| Monomer III | 3.1 | 8.5 | 9.6 |
| Copolymer 7 | 3.2 | 8.7 | 9.9 |
| Copolymer 8 | 2.9 | 8.6 | 9.8 |
| Copolymer 9 | 2.9 | 8.4 | 9.8 |

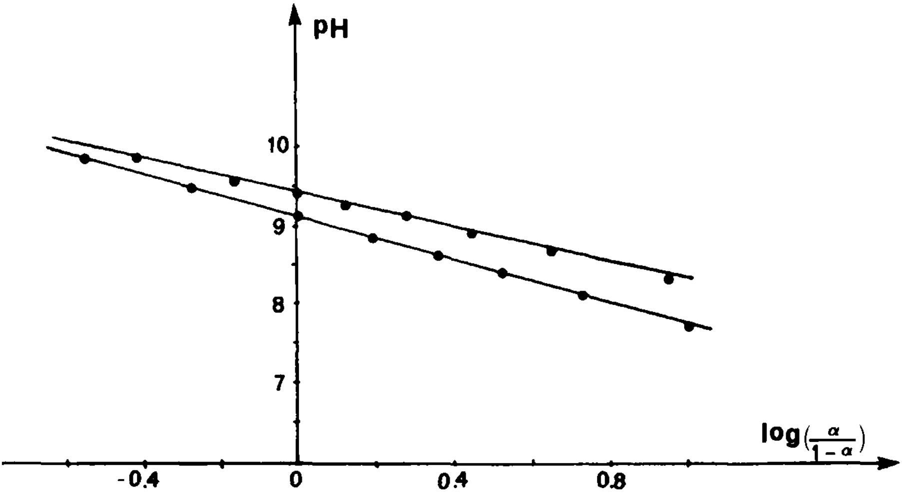


FIG. 5. Plot of pH versus log [$\alpha/(1 - \alpha)$] for Copolymer 9. Top curve: In water (slope 1.4). Bottom curve: In 1 *M* NaCl (slope 1.0).

dence of the interaction between the cationic sites during ionization. This effect is canceled by the addition of NaCl, and the slope becomes unity.

The determination of the acidity constants for the other copolymers is easier because there is only one amine group per monomeric unit, and these constants can be computed simply from the titration curve at the point of half neutralization. A sample titration curve of a copolymer is shown in Fig. 6, and the following p*k*s were obtained (in 1 *M* NaCl): 9.8 (Sample 1), 10.2 (2), 10.1 (3), 10.3 (4). Little influence of the copolymer composition on the acidity constant of the amine site was observed.

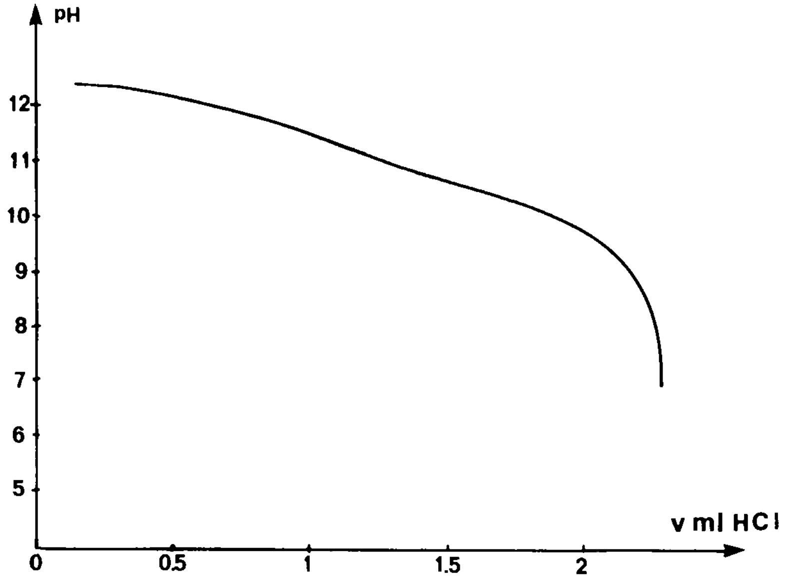


FIG. 6. Titration curve for Copolymer 4 ($C_p$ = 10 meq/L) in 1 *M* NaCl with 0.5 *N* HCl.

In conclusion, as expected, only the copolyammonium salts which have high charge densities show a significant interaction between neighboring cationic sites.

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