

Synthesis and solution properties of water soluble copolymers based on acrylamide and quaternary ammonium acrylic comonomer

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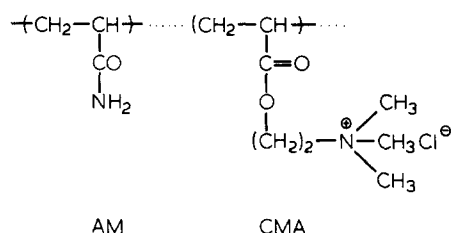
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We have prepared cationic polyelectrolytes with a large range of compositions by the redox polymerization and copolymerization of acrylamide and (*N,N,N*-trimethyl) aminoethyl chloride acrylate. Molecular weights of the various samples were determined by light scattering, and the intrinsic viscosities of these polymers measured in aqueous solutions of various ionic strengths. We propose empirical laws between viscosity, composition in comonomers, molecular weight and ionic strength. Results also give the radius of gyration of macromolecules in NaCl solution (between 10^{-2} M and 1 M).

(Keywords: polyacrylamide derivatives; cationic flocculants; water soluble polymers)

The use of polyelectrolytes based on acrylamide is of increasing interest in the fields of ore separation and waste treatment^{1,2}. In the range of copolymers with cationic charges, the corresponding structures are generally obtained by redox polymerization, but their stability in aqueous solution and the relationships between molecular weight, viscosity and ionic strength are not yet well known.

The homopolymers and copolymers of acrylamide (AM) and (*N,N,N*-trimethyl) aminoethyl chloride acrylate (CMA), were prepared in order to study their flocculation properties.



If m and n are respectively the number of AM and CMA units in the macromolecules of these random copolymers the cationicity, τ , is given by the relation $\tau = n/n + m$. Various compositions and molecular weights (from some thousands to some millions) were obtained. The samples were studied by light scattering and viscometry in aqueous solutions of various ionic strength.

Synthesis

Pure grade monomers were kindly provided by 'Société Française Hoechst'. Redox polymerization was performed in water with ammonium persulphate/sodium metabisulphite as initiator. The copolymer compositions were

adjusted according to the comonomer ratios. They had very homogeneous monomer unit repartitions which was in good agreement with their copolymerization reactivity ratios (close to 1)³. A very large range of molecular weights was obtained by convenient choice of monomer and initiator concentrations. The experimental conditions are summarized in Table 1. For the (AM-CMA) 30% copolymers (that is $\tau = 0.3$); 24.8 g of acrylamide (0.35 mole) and 28.6 g of CMA (0.15 mole) were dissolved in 300 ml of deionized water (in a half-litre stirred reactor). The pH was adjusted to 4.5 by adding sulphuric acid (preventing hydrolysis of amide or ester functions). Dissolved oxygen was removed by bubbling nitrogen for the duration of the polymerization. Ammonium persulphate (in 15 ml of water) and sodium metabisulphite were successively introduced (with stirring). The temperature rose from 20° to 28°C in $\frac{1}{2}$ h and then began to decrease. The reactor was then heated for 2 h at 80°C. The cooled solution (diluted by water if very viscous) was poured into acetone and the polymer, free of monomers and oligomers, recovered by filtration. The crude product was dried for 24 h (room temperature 0.1 mm Hg), milled and dried again for 24 h. The yield was about 90%.

Polymers of the acrylamide type are hygroscopic⁴⁻⁸. For copolymers of (AM-CMA) (I), a freeze dried sample was not free of water even after some hours of drying with a diffusion pump. Its weight increased 2.5% in 1 h if left in the open air. The rate of moisture adsorption then decreased and becomes very slow for about 10% adsorbed water. This value remains stable over several months when samples are carefully enclosed. On the other hand a thermogravimetric study (Setaram type balance) showed that complete drying does not occur before chain degradation (in a nitrogen atmosphere as well as in vacuum).

Microanalysis of polyacrylamide samples (Table 2) reflects their hydroscopic character: the N/C ratio is correct but the ratio of oxygen and hydrogen are consistent with a moisture content, calculated from the shift of the carbon ratio between theoretical and experimental

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Table 1 Experimental conditions

Name	Total monomer concentration (mol ⁻¹)	$\pi = \frac{n}{n+m}$	(NH ₄) ₂ S ₂ O ₈ (mol ⁻¹)	Na ₂ S ₂ O ₅ (mol ⁻¹)
PAM II	1.5	0	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
PAM III	1.5	0	9.50 × 10 ⁻⁵	6.90 × 10 ⁻⁵
PAM IV	1.5	0	1.84 × 10 ⁻⁴	1.36 × 10 ⁻⁴
PAM V	1.5	0	2.75 × 10 ⁻⁴	2.04 × 10 ⁻⁴
PAM VI	1.5	0	4.59 × 10 ⁻⁴	3.40 × 10 ⁻⁴
PAM VII	1.5	0	1.14 × 10 ⁻³	8.51 × 10 ⁻⁴
PCMA I	1.5	1.0	4.59 × 10 ⁻⁴	3.40 × 10 ⁻⁴
PCMA II	1.5	1.0	1.48 × 10 ⁻⁴	1.10 × 10 ⁻⁴
PCMA III	2.0	1.0	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
PCMA IV	1.0	1.0	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
PCMA V	1.7	1.0	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
PCMA VI	1.0	1.0	3.44 × 10 ⁻³	2.54 × 10 ⁻³
Cop(AM-CMA)30%I	1.5	0.30	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)30%II	2.0	0.30	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)30%III	1.0	0.30	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)30%VI	2.5	0.30	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)30%VII	0.5	0.30	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)30%VIII	0.75	0.30	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)5%I	1.5	0.04	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)5%II	1.5	0.05	9.18 × 10 ⁻³	6.81 × 10 ⁻³
Cop(AM-CMA)15%	1.5	0.15	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)50%	1.5	0.50	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)80%	1.5	0.80	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴
Cop(AM-CMA)65%	1.5	0.65	4.74 × 10 ⁻⁴	3.47 × 10 ⁻⁴

Table 2 Polyacrylamide analysis

	% C	% H	% O	% N	N/C	$\frac{C_{exp.}}{C_{theo}}$	% O calc	% H calc
% Theor.	50.70	7.04	22.54	19.72	0.389	1	—	—
% Exp.								
PAM II	46.91	7.14	27.51	18.23	0.389	0.925	27.52	7.35
PAM III	45.33	7.60	29.04	17.34	0.383	0.894	29.57	7.47
PAM IV	46.93	7.48	26.62	18.51	0.397	0.926	27.45	7.34
PAM V	47.15	7.73	27.54	18.01	0.382	0.930	27.19	7.32
PAM VI	46.38	7.55	28.04	18.40	0.397	0.915	28.18	7.39
PAM VII	45.77	7.63	28.85	17.75	0.390	0.903	28.98	7.43

Table 3 Analysis of polyCMA

	%C	%H	%O	%N	%Cl	N/C	N/Cl	$\frac{Cl_{exp.}}{Cl_{theo}}$	%O calc	%H calc
% Theo.	49.61	8.27	16.54	7.23	18.34	0.146	0.394	1	—	—
% Exp.										
PCMA I	45.28	8.74	23.14	6.50	16.44	0.143	0.395	0.896	22.83	8.52
PCMA II	42.52	8.50	25.60	6.29	16.04	0.143	0.392	0.874	25.66	8.63
PCMA III	41.66	8.54	25.82	6.39	16.26	0.153	0.393	0.886	24.79	8.59
PCMA IV	44.74	8.64	23.81	6.35	16.78	0.142	0.378	0.915	22.79	8.51
PCMA V	43.12	8.51	25.73	6.40	16.41	0.148	0.390	0.895	24.24	8.57
PCMA VI	44.76	8.79	22.56	6.30	16.48	0.141	0.382	0.899	23.85	8.55

values. Similar results are observed with homopolymers and copolymers of CMA (Tables 3 and 4) where the N/C and N/Cl ratios are unaffected by the presence of moisture. So for all our physico-chemical measurements we preferred to use samples treated at room temperature, taking into account, of course, their water content. For the copolymers (Table 4), values of τ , calculated from nitrogen and chlorine contents, are close to the initial monomer ratios. In all cases, ¹³C n.m.r. spectra (Jeol PS 103) of 5% polymer in aqueous solutions (NaCl 1M) led to the

expected structure, with the absence of carbonated impurities.

Viscometry

Mother liquor solutions ($C_0 \approx 0.1\%$) were prepared by very slow dissolution (magnetic stirring of the polymer samples) for 24 h, in an unfiltered solution of 1M NaCl. By convenient dilutions, five solutions were obtained ($C_0, 4C_0/5, 3C_0/5, 2C_0/5, C_0/5$). They were centrifuged for 2 h, at 20 000 g, before use in light scattering experiments; the

Table 4 Analysis of copolymers

	%C	%H	%O	%N	%Cl	N/Cl	%r	$\frac{\%Cl_{\text{exp}}^-}{\%Cl_{\text{theo}}^-}$
Cop(AM-CMA)30%I	47.73	8.01	24.76	11.22	8.72	1.29	30.5	0.864
Cop(AM-CMA)30%II	47.37	8.00	25.00	11.75	9.01	1.30	30.2	0.893
Cop(AM-CMA)30%III	46.48	8.13	27.38	10.45	8.15	1.28	30.7	0.808
Cop(AM-CMA)30%VI	44.46	8.31	27.46	10.88	8.86	1.23	32.1	0.878
Cop(AM-CMA)30%VII	47.95	8.22	24.22	12.26	9.43	1.30	30.2	0.935
Cop(AM-CMA)30%VIII	45.64	8.59	24.85	11.88	9.35	1.27	31.0	0.927
Cop(AM-CMA)I 5%	47.70	7.53	26.06	16.31	2.00	8.15	4.8	0.903
Cop(AM-CMA)III 15%	47.09	7.31	28.05	16.10	1.57	10.25	3.8	0.880
Cop(AM-CMA)15%	46.28	8.27	25.93	14.88	5.57	2.67	14.8	0.935
Cop(AM-CMA)50%	42.49	8.11	27.89	9.28	11.87	0.78	50.4	0.892
Cop(AM-CMA)65%	44.05	8.28	28.65	7.74	12.14	0.64	62.9	0.804
Cop(AM-CMA)80%	43.68	9.20	25.65	7.18	14.53	0.49	79.8	0.865

same samples were also used for intrinsic viscosity measurements. In NaCl solution with an addition of 50 ppm of a bactericide (Procida 109 provided by 'Roussel Uclaf' Co.), the viscosity of these polymers slowly decreased (about 2% for PAM and PCMA in 5 days and 10% in 30 days at 25°C for 0.1% solutions). The stability is compatible with the duration of complete physico-chemical measurements.

The shear rate (G) behaviour of polyacrylamide type polymer solutions is classical. The viscosity, constant for the low values of G , progressively decreases when G increases⁸⁻¹⁴. This evolution is in correlation with the coil deformation in the flow. For instance the viscosity of a 0.1% polyCMA solution (polymer: PCMA V, $\bar{M}_w \approx 3.5 \times 10^6$, solution: NaCl 1M) is stable for G lower than a critical value $G_c = 300 \text{ s}^{-1}$, and then progressively decreases for higher values of G , the decrease is 7% for $G = 1300 \text{ s}^{-1}$. As this discrepancy decreases with the polymer dilution, the intrinsic viscosity measured with classical Ostwald viscometers (G range 1000-1400 s^{-1}) is practically unaffected (in our samples where measurements were performed by successive dilutions of a 0.1% solution). This can be verified through a practically linear variation observed by plotting the reduced or inherent viscosity versus the polymer concentration. In the same way the plot of $\log[\eta]/\log M$ is a straight line. However, for polymers of molecular weight larger than our samples, a deflexion would probably be observed because G_c strongly increases with the molecular weight. For such samples the $[\eta]-M$ relation should be used only if $[\eta]$ was measured with a low shear apparatus.

Light scattering

Polymer solutions were prepared as previously indicated. We checked that the scale of concentration used (0.1% to 0.02%) was convenient; a complementary dilution (between 0.02% and 0.004%) leads to a Zimm plot with the same extrapolated values. Measurements were performed with a Sofica 42000 photogonio-diffusometer and a differential refractometer Brice-Phoenix for $\lambda = 546.1 \text{ nm}$. The refractive index increments are:

PAM VI	0.175 ml/g
Copolymer (AM-CMA) I	0.166 ml/g
PCMA I	0.154 ml/g

For polyacrylamide they agree with the published data^{5,8,13-15}. We observed that the dn/dc values apparently vary linearly according to the CMA content in copolymers. As the repartition in the chain of the two types of units may be considered as statistical, light-scattering leads to true values of the copolymer molecular weights and not to apparent ones¹⁶⁻¹⁷.

An example of a Zimm plot is given in Figure 1, the most probable location of the extrapolated straight lines ($\theta \rightarrow 0$ and $c \rightarrow 0$) are obtained by using a Hewlett Packard 9825 minicomputer.

In Table 5, the mean molecular weights (\bar{M}_w) as well as radius of giration ($\langle R_G^2 \rangle$) and the second virial coefficient A_2 . These values lead to the $\langle R_G \rangle/\bar{M}_w$ relationships:

$$\begin{aligned} \text{PAM} & \langle R_G^2 \rangle^{1/2} (\text{\AA}) = 0.56 \bar{M}_w^{0.50} \\ \text{(AM-CMA) 30\% Copolymer} & \langle R_G^2 \rangle^{1/2} (\text{\AA}) = 0.33 \bar{M}_w^{0.54} \\ \text{PCMA} & \langle R_G^2 \rangle^{1/2} (\text{\AA}) = 0.45 \bar{M}_w^{0.51} \end{aligned}$$

Viscosity-molecular weight relationships

NaCl 1M solutions. A Mark-Houwink type law $[\eta] = k.M^a$ was found according to \bar{M}_w and viscosity measurements described previously (25°C, NaCl 1M). A linear regression law applied to data of Figure 5 leads to:

$$\text{PAM: } [\eta]_{\text{dl/g}}^{25^\circ\text{C, NaCl 1M}} = 1.91 \times 10^{-4} \bar{M}_w^{0.71}$$

$$\text{Copolymer (AM-CMA) 30\%: } [\eta]_{\text{dl/g}}^{25^\circ\text{C, NaCl 1M}} = 1.05 \times 10^{-4} \bar{M}_w^{0.73}$$

$$\text{PCMA: } [\eta]_{\text{dl/g}}^{25^\circ\text{C, NaCl 1M}} = 0.23 \times 10^{-4} \bar{M}_w^{0.82}$$

These relationships were found for samples with molecular weights between 5×10^5 and 5×10^6 .

For polyacrylamide, other laws have already been published^{5,8,13,15,18-20} with a values lying between 0.66 and 0.77. But direct comparison is not easy because experimental conditions such as temperature, ionic strength of the solvent or composition of the sample (fractionated or not) may differ. In fact, the drawing of a complete diagram, such as Figure 2 (drawn with all the proposed relationships), shows that these laws closely adhere for large range molecular weights, because large values of a are balanced by low values of K . The law that we have found is very close to the results recently

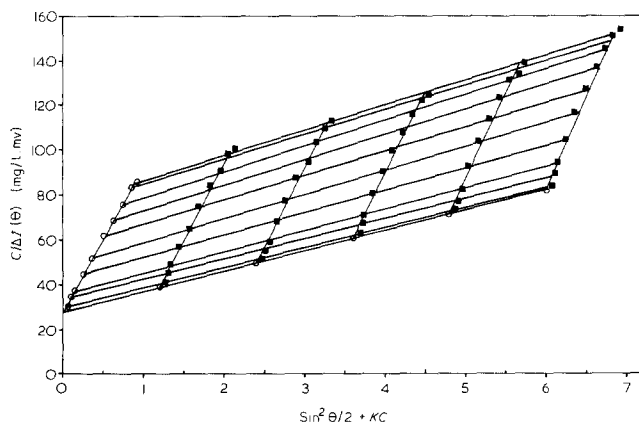


Figure 1 Zimm plot of a copolymer sample: Copoly(AM-CMA) 30%, solution NaCl 1M, room temperature, $K=0.006$ l/mg

Table 5 Light scattering results

	\bar{M}_w	$(R_G^2)^{1/2}$ (Å)	A_2 (mol ml g ⁻²)
Polyacrylamide			
PAM VI	4.9×10^5	410	8.5×10^{-5}
PAM V	1.2×10^6	680	7.3×10^{-5}
PAM II	2.0×10^6	850	6.5×10^{-5}
PAM III	2.9×10^6	985	3.6×10^{-5}
PAM IV	3.2×10^6	1085	4.7×10^{-5}
30% CMA copolymers			
Cop(AM-CMA)VII	4.5×10^5	350	3.8×10^{-4}
Cop(AM-CMA)VIII	5.8×10^5	425	4.2×10^{-4}
Cop(AM-CMA)III	1.4×10^6	695	3.8×10^{-4}
Cop(AM-CMA)I	1.4×10^6	665	3.8×10^{-4}
Cop(AM-CMA)VI	2.3×10^6	880	3.9×10^{-4}
Cop(AM-CMA)II	2.7×10^6	920	4.5×10^{-4}
CMA homopolymers			
PCMA I	8.5×10^5	470	2.4×10^{-4}
PCMA IV	1.6×10^6	580	3.0×10^{-4}
PCMA V	3.4×10^6	885	2.4×10^{-4}
PCMA III	5.1×10^5	1160	1.9×10^{-5}

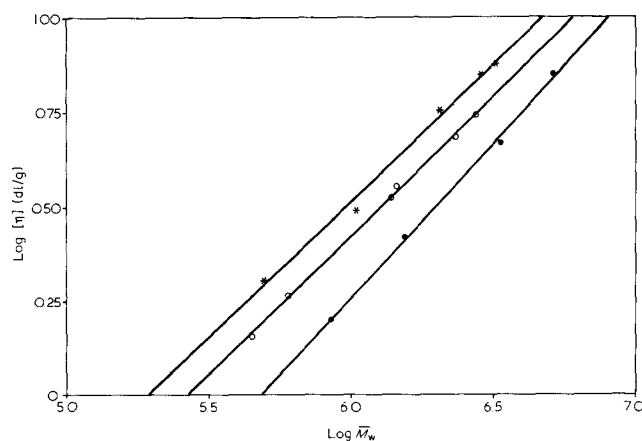


Figure 2 Relationship between intrinsic viscosity $[\eta]$ (25°C, NaCl 1 M) and mean molecular weight (\bar{M}_w). * PAM
○ Cop(AM-CMA) 30%; ● PCMA

published by Kulicke *et al.*²⁰ based on 8 carefully prepared polyacrylamide samples with $\bar{M}_w/\bar{M}_n=2.5$, in 0.1M Na₂SO₄ solution: $[\eta]_{dl/g}^{25^\circ C} = 1.94 \bar{M}_w^{0.70}$. For homopolymers and copolymers of CMA, values of a do not suggest a typical behaviour of rodlike polymers but instead a flexible coil behaviour.

We have also used the Stockmayer-Fixman relationship²¹:

$$[\eta] = X\sqrt{\bar{M}_w} + Y\bar{M}_w$$

which is more able to conveniently express the effect of the ionic strength.

	X	Y	$([\eta])$ in dl/g
PAM	$2.28 \cdot 10^{-3}$	$1.12 \cdot 10^{-6}$	"
Copolymer (AM-CMA) 30%	$1.44 \cdot 10^{-3}$	$1.15 \cdot 10^{-6}$	"
PCMA	$8.0 \cdot 10^{-4}$	$1.01 \cdot 10^{-6}$	"

Effect of the ionic strength. The intrinsic viscosity of our samples was studied in sodium chloride solution for salt concentration (C_s) between 10^{-2} mol l⁻¹ and 1 mol l⁻¹. For polyacrylamide, as previously observed²², the viscosity is practically independent of the ionic strength.

The intrinsic viscosity of polyelectrolytes is often expressed by the general law^{23,24}.

$$[\eta] = K_1 + K_2 \frac{1}{\sqrt{C_s}}$$

In fact, in our case, no linear relationship between $[\eta]$ and $C_s^{-1/2}$ is observed and an empirical variation with a complementary term gives best results (see Figure 3):

$$[\eta] = \alpha + \frac{\beta}{\sqrt{C_s}} + \frac{\gamma}{C_s}$$

The discrepancy towards a linear variation in $C_s^{-1/2}$ for low ionic strength might be interpreted, as a semi-rigid

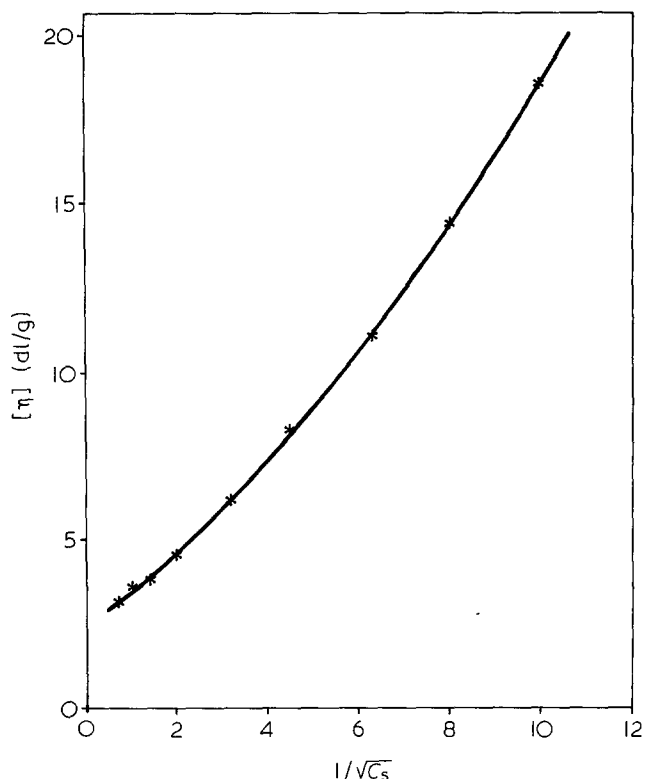


Figure 3 Evolution of the intrinsic viscosity of copolymer Cop(AM-CMA) $\tau=0.3$ versus the ionic strength of NaCl solutions. (The salt concentration C_s takes into account the polymer's own ions)

configuration. This would occur for polyelectrolytes in very dilute salt solution or by a deformation of the ionic atmosphere surrounding the macromolecules in an hydrodynamic flow. However, these arguments do not appear convincing since, in the same scale of ionic strength, polyelectrolytes of similar structure, especially hydrolysed polyacrylamides, lead to a linear relationship $[\eta] - C_s^{-1/2}$. The peculiar behaviour of our samples might be explained in terms of the bulkiness of the side substituents (trimethylaminoethyl chloride) in the vinylic backbone. These would hinder the free flowing of solvent molecules around the chains. In a recent theory²⁵ Imai showed that the viscosity of polyelectrolytic solutions is altered by a factor C_s^{-1} when the coils are impenetrable to solvent molecules in a flow and a $C_s^{-1/2}$ factor when they are completely permeable. By combining $[\eta] = f(\bar{M}_w)$ law in the Stockmayer-Fixman form and $[\eta] = f(C_s)$ above, we suggest an empirical relationship $[\eta] = f(C_s, \bar{M}_w)$ in the form:

$$[\eta] = (\beta' + \beta'' C_s^{-1/2}) \bar{M}_w^{1/2} + (\gamma' + \gamma'' C_s^{-1}) \bar{M}_w$$

For a given copolymer composition, the coefficients β' , β'' , γ' and γ'' can easily be deduced from two series of experiments (which correspond to full line curves in Figure 4). First, viscosity measurements were carried out at a constant ionic strength and various molecular weights and secondly, studies of the viscosity in various salt solutions for a sample of given molecular weight were carried out.

For instance, for $\tau = 30\%$ we found:

(AM-CMA) 30% Copolymer

$$[\eta]_{dl/g}(\bar{M}_w, C_s) = (5.18 \cdot 10^{-4} + 8.42 \cdot 10^{-2} C_s^{-1/2}) \bar{M}_w^{1/2} + (1.11 \cdot 10^{-6} + 4.03 \cdot 10^{-8} C_s^{-1}) \bar{M}_w$$

This formula leads to the intrinsic viscosity of a sample for any value of the molecular weight and salt concentration (broken lines in Figure 4). For PCMA the calculated curve $[\eta] = f(C_s)$ for (AM-CMA) 30% Copolymer $\bar{M}_w = 580\,000$ fits very well with experimental data (as well as $[\eta] = f(\bar{M}_w)$ in 10^{-2} M NaCl (see Figure 5). For other copolymers we also determined $[\eta]$ at 25°C:

(AM-CMA) 5% Copolymer

$$[\eta]_{dl/g} = (1.85 \cdot 10^{-3} + 2.31 \cdot 10^{-4} C_s^{-1/2}) \bar{M}_w^{1/2} + (1.09 \cdot 10^{-6} + 2.07 \cdot 10^{-3} C_s^{-1}) \bar{M}_w$$

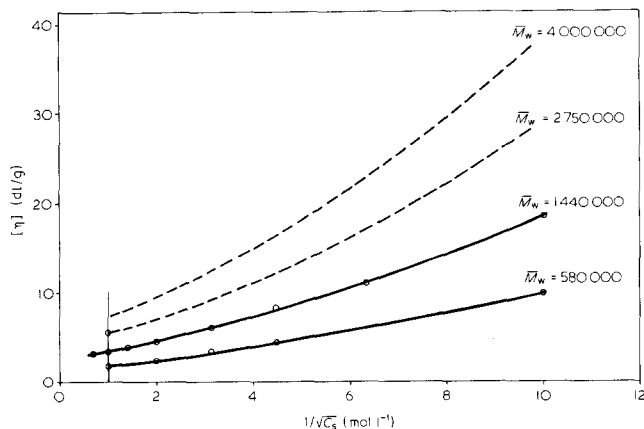


Figure 4 Intrinsic viscosities of copolymers (AM-CMA) $\tau=0.3$ versus the salt concentration C_s of their NaCl aqueous solution (25°C). —○, ○: experimental data; ---, ○ calculated data

(AM-CMA) 15% Copolymer

$$[\eta]_{dl/g} = (9.75 \cdot 10^{-4} + 8.92 \cdot 10^{-4} C_s^{-1/2}) \bar{M}_w^{1/2} + (1.06 \cdot 10^{-6} + 1.10 \cdot 10^{-8} C_s^{-1}) \bar{M}_w$$

(AM-CMA) 50% Copolymer

$$[\eta]_{dl/g} = (2.52 \cdot 10^{-4} + 1.08 \cdot 10^{-3} C_s^{-1/2}) \bar{M}_w^{1/2} + (9.20 \cdot 10^{-7} + 1.64 \cdot 10^{-8} C_s^{-1}) \bar{M}_w$$

$$\text{PCMA } [\eta]_{dl/g} = (-8.3 \cdot 10^{-5} + 8.83 \cdot 10^{-4} C_s^{-1/2}) \bar{M}_w^{1/2} + (1.00 \cdot 10^{-6} + 1.10 \cdot 10^{-8} C_s^{-1}) \bar{M}_w$$

Effect of the CMA ratio. The equations above, allow us to compare the evolution of $[\eta]$, for a polyelectrolyte with a given mean polymerization degree, versus CMA ratio in the chains (for various values of C_s). Results, given in

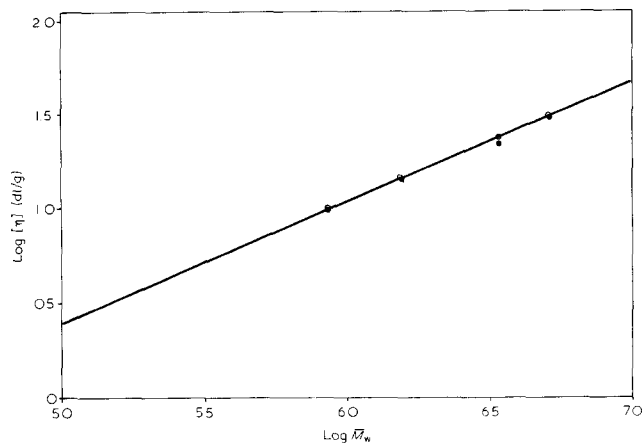


Figure 5 Intrinsic viscosity/molecular weight (\bar{M}_w) relationship for homopolymers of CMA in NaCl 10^{-2} M at 25°C. ○ calculated; ● experimental

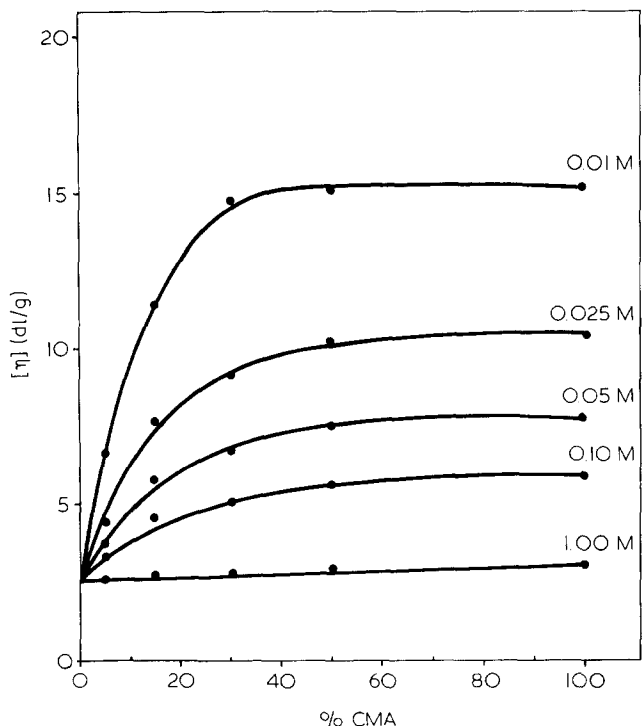


Figure 6 Evolution of the intrinsic viscosity of (AM-CMA) copolymers of a given polymerization degree ($DP_w = 10^4$), versus the CMA content of the polymers in salt solutions of various ionic strengths

Figure 6, indicate that the viscosity is practically independent of τ for high ionic strengths. For low concentration salt solutions, $[\eta]$ greatly increases when τ grows from 0 to about 30% and becomes stable for higher values of τ . Such behaviour may be explained if we consider, (according to the Manning theory^{26,27}) that an increasing number of counterions may be condensed on the ammonium sites when τ exceeds a given value. This value ($\approx 0.3\%$) may also be suggested by conductimetric measurements^{4,28}.

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