Characterization of high charge density ampholytic copolymers prepared by microemulsion polymerization

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A series of copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and 2-methacryloyloxyethyltrimethylammonium chloride (MADQUAT) prepared by microemulsion polymerization was characterized by means of several techniques. After dialysis, the samples self-neutralize with formation of monomer pairs in the copolymer. The molecular weights determined by light scattering are high ($\geqslant 10^7$) and were found to be relatively unaffected by monomer feed ratios. The copolymer microstructure was calculated from the reactivity ratios and compared to that obtained for copolymers synthesized in aqueous solution. The microemulsion polymerization process yields copolymers more homogeneous in composition ($r_A r_B \simeq 1.6$) than those obtained by polymerization in solution which have a strong tendency to alternation ($r_A r_B \simeq 0.05$). These differences are discussed in terms of microenvironment and polymerization mechanisms.

(Keywords: microemulsion polymerization; polyampholytes; methacryloyloxyethyltrimethylammonium chloride polymerization; sodium 2-acrylamido-2-methylpropanesulfonate polymerization; reactivity ratios for polyampholytes)

INTRODUCTION

In recent years, we have begun a detailed investigation into the synthesis as well as the characterization and solution properties of water-soluble polymers prepared by inverse microemulsion polymerization[1–3]. The process was shown to lead to remarkably stable, clear microlatexes of low-particle size containing up to 25% of high-molecular-weight polymers in the medium, in contrast to inverse latexes prepared by using classical emulsions that are often unstable and turbid.

The (co)polymerization of the following monomers in microemulsions has been thoroughly investigated: neutral monomer (acrylamide)[1,2,4]; anionic (sodium acrylate)[5]; cationic (2-methacryloyloxyethyltrimethylammonium chloride)[6]. In our continuing research on water-soluble polymers, we have recently extended the process to the synthesis of copolymers which possess both positively and negatively charged moieties along the macromolecular backbone, i.e. polyampholytes. The introduction of these ionic groups into the polymer chain results in a complex solution behaviour which is essentially controlled by electrostatic interactions[7,8]. These are influenced by a number of parameters such as the number and the nature of the ionic sites, the pH or the ionic strength. In particular, a polyampholyte with a balanced stoichiometry shows antipolyelectrolyte solution behaviour, e.g. low water-solubility but increased solubility and enhanced viscosity upon adding salt.

In spite of their great interest for potential applications, only a few studies were conducted on ampholytic polymers[7–12], particularly on polyampholytes possessing dissimilar charge ratios.

This paper is part of a series devoted to high-charge-density polyampholytes formed from sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) and 2-methacryloyloxyethyltrimethylammonium chloride (MADQUAT). In part I[13], the synthesis of compositionally tailored polyampholytes is described with special emphasis given to a search for an optimal formulation of the microemulsions compatible with an economical process. Part II[14] concerns the investigation of their aqueous solution properties by turbidimetry and viscometry experiments. The results are well accounted for by a recent theory of Higgs and Joanny[15]. In the present work, we report on the characterization of the ampholytic series prepared by microemulsion polymerization.

The copolymer composition, charge distribution, density, molecular weight and microstructure are determined and examined in detail. The knowledge of these parameters is essential for a comprehensive analysis of the structure–solution–properties relationships. In particular, an unanswered question remains regarding the influence of the microstructure on the solution properties. In general, polyampholytes prepared in aqueous solution exhibit a tendency for alternation[9,16] as a result of the strong electrostatic attractive forces which are operative between the oppositely charged monomers. However, it is well recognized that the microenvironment has a strong influence on the free-radical copolymerization of ionic monomers[17,18]. For example, copolymerization of acrylamide (AM) and sodium acrylate (NaA) in microemulsions was shown to lead to random copolymers with reactivity ratios close

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to unity[19], values significantly different from those obtained for the same copolymers in solution: $r_{NaA} \simeq 0.3$; $r_{AM} \simeq 0.95$.

In order to gain further insight into the effect of the reaction medium on the copolymer microstructure, two complementary series of polyampholytes of variable composition were prepared in fresh water and aqueous salt solution, respectively. The monomer reactivity ratios were determined and compared with those obtained for the same polyampholytes prepared in microemulsions. The results are presented below and the effect of the microenvironment on the monomer sequence distribution is discussed in view of other literature data.

EXPERIMENTAL

Materials

2-Methacryloyloxyethyltrimethylammonium chloride (MADQUAT) was supplied by Elf-Aquitaine as a 75% w/w aqueous solution. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS), obtained from Cassella, was recrystallized from dry methanol prior to use. Neutralization at pH $\simeq$ 9 was achieved by slow addition of AMPS to an aqueous sodium hydroxide solution. Water was double-distilled. The hydrophobic initiator AIBN (2,2'-azobisisobutyronitrile) was recrystallized from ethanol and dried under vacuum. The oil is a narrow-cut isoparaffinic mixture, Isopar M from Esso Chemie, which was filtered before use (boiling range 207–275°C). The emulsifier is a blend of sorbitan sesquioleate (Arlacel 83, HLB: hydrophile–lipophile balance $\simeq$ 3.7) and of sorbitan monooleate with 20 ethylene oxide residues (Tween 80, HLB $\simeq$ 15), supplied by ICI Speciality Chemicals.

The transparent and thermodynamically stable microemulsions were prepared with stirring by adding the aqueous solution of monomers (adjusted to pH $\simeq$ 7) to the mixture of emulsifiers, AIBN and Isopar M. The recipe used was the following (w/w): Isopar M, 44%; monomers, 22%; water, 22%; non-ionic emulsifiers, 12%. More details on the formulation of these polymerizable microemulsions are given elsewhere[13].

Polymerization procedure

The microemulsion polymerization experiments were carried out in water-jacketed reaction vessels after bubbling purified nitrogen through the microemulsion to eliminate oxygen. The monomer feed was initiated with AIBN as the oil-soluble initiator (0.3 wt% based on monomers) by irradiation at 20°C with ultra-violet light (mercury lamp, Philips).

Total conversion of copolymer was achieved within less than 30 min. The product of the polymerization was a clear and stable microlatex[13]. After polymerization, the latexes were poured into an excess of 2-propanol and the precipitated copolymers were separated and washed several times. They were then filtered and dried under vacuum at 45°C. Conversions were determined gravimetrically.

In the case of polymerization reactions conducted in homogeneous aqueous solution (pH = 7.0), the monomer feed (0.45 M) was initiated thermally ($T = 45$°C) with potassium persulfate (0.1 mol% based on monomers).

In the case of polymerizations to be stopped at low-conversion levels, the reaction was stopped at the appropriate point by precipitation of the solution or the latex in an excess of 2-propanol maintained at 5°C and containing hydroquinone inhibitor.

In order to eliminate impurities (monomer, residual salt, emulsifiers, etc.) the polymer powders (low- and high-conversion samples) were subsequently dissolved in 1 M NaCl aqueous solutions and dialysed against deionized water before recovering by freeze-drying.

In the following, pNaAMPS and pMADQUAT refer to the homopolymers and Ax/My to a copolymer containing x and y mol% of NaAMPS and MADQUAT, respectively.

Copolymer characteristics

Molecular composition. The composition of ampholytic polymers was determined by elemental analysis on both the low- and high-conversion samples. The weight percentages of C, H and N were determined with a Carlo Erba Elemental Analyzer, the sodium content by atomic absorption spectrophotometry and Cl, N and S by mineralization using the Schöninger method.

The water content in the copolymer was measured by Karl Fischer's method with an automatic KFE452 titrimeter.

^{13}C n.m.r. spectroscopy. ^{13}C n.m.r. spectra for the A50/M50 copolymer and the homopolymers were obtained at 50 MHz on a Brüker spectrometer using 5 wt% aqueous (D_2O) polymer solutions. The deuterated water contained salt to ensure copolymer dissolution (1.2 M NaCl) or to decrease the solution viscosity of the homopolymers (0.5 M NaCl).

I.r. spectroscopy. I.r. spectra were obtained using a Perkin-Elmer 983 spectrophotometer. The samples were dissolved in aqueous solution and the polymer films were obtained on an Irtran-2 pellet by water evaporation for several days at room temperature.

Density experiments. Partial-specific-volume ($\bar{v}$) measurements were carried out at 25°C with an automatic densitometer of PAAR DMA 60 type on non-dialysed dilute samples ($2 \times 10^{-3} < C < 1.5 \times 10^{-2}$ g cm^{-3}) in fresh water for the homopolymers and in NaCl aqueous solutions for the copolymers (accuracy of $\bar{v}$: $\pm 10^{-3}$ cm^3 g^{-1}).

Light-scattering (LS) experiments. The molecular weights of the polymers were determined using an AMTEC SM 200 spectrophotometer. The optical source was a helium-neon laser operating at 632.8 nm.

As polyampholyte solutions are very sensitive to shear degradation and to aggregation, the polymer stock solutions were made by dissolving the polymer at very low concentration ($\simeq 5 \times 10^{-5}$ g cm^{-3}) in NaCl aqueous solutions with gentle stirring, 48 h before the measurements.

The salt concentration was 1.0 M NaCl for the homopolymers. For copolymers, on addition of salt, the solubility in water varies in a complex way as shown in another paper of this series[14]. Consequently, a 2.0 M NaCl concentration was selected for which all the samples had been observed to be soluble. The solutions were then diluted to appropriate concentrations (down to 10^{-5} g cm^{-3}) and were made dust-free by centrifugation. The refractive index increments, dn/dc, were determined on dilute samples in NaCl aqueous solutions ($2\times10^{-3} < C < 1\times10^{-2}$ g cm^{-3}) with a Brice-Phoenix differential refractometer (wavelength, $\lambda = 632.8$ nm).

The samples are hygroscopic and, for all experiments, the concentrations were corrected for water content.

RESULTS

Polymer macrostructure

Homopolymers. The elemental analysis data obtained for the homopolymers are given in *Table 1*. The theoretical values ascribed to the different elements were corrected for water content. A fairly good agreement is observed between the experimental and calculated values, although a systematic excess of C, H and O is observed along with a deficiency of the other elements. These deviations may be related to a partial hydrolysis of the ester and amide groups and/or to some surfactants' adsorption (these are formed from C, H and O) on the polymers. However, the low values of the degree of hydrolysis ($\leqslant 3\%$ *Table 2*), as determined by titration of the –COO groups, and the small deviations observed suggest that these two effects are rather limited.

In *Table 2* the values of some characteristic ratios relative to each homopolymer are also reported: (% N/14)/(% Cl/35.5) for MADQUAT and (% N/14)/(% S/32.1) and (% Na/23)/(% S/32.1) for pNaAMPS. The ratios are close to the theoretical value of one. This self-consistency is clear evidence of the reliability of the N, S, Cl and Na elemental analysis data on which the copolymer composition is based.

It should also be noted that no difference was observed in the data relative to dialysed and non-dialysed samples. This is an indication that the recovery of the copolymer by simple precipitation in 2-propanol followed by several washings is sufficient to provide samples free of impurities.

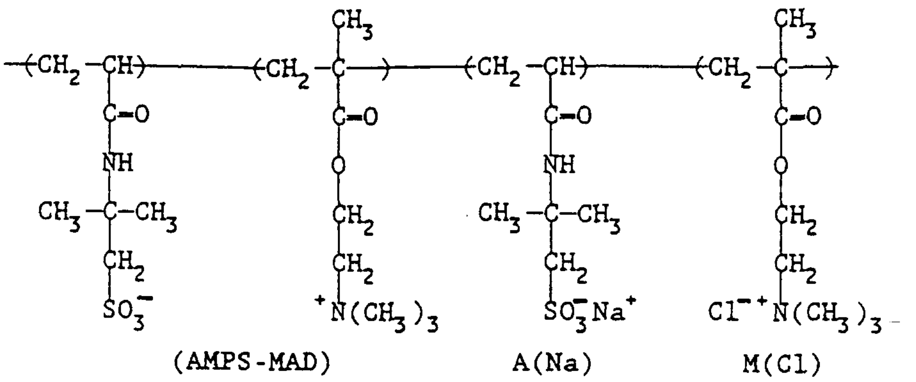
Copolymers. The molar fraction of NaAMPS in the copolymer, F_A, was calculated from % S and % N data according to the following equation:

$$F_A = \frac{n_A}{n_A + n_M} = \frac{14.0}{32.1} \times \frac{\%\,S}{\%\,N} \qquad (1)$$

where n_A and n_M are the number of moles of NaAMPS and MADQUAT in 100 g sample, respectively. Equation (1) does not take into account the presence or absence of inorganic counterions. The charged units of polyampholytes may indeed pair with their inorganic counterions or with the oppositely charged mer unit with a loss of Na^+ and Cl^- ions. Therefore, the macromolecular chain can be formed of the repeating units shown in *Scheme 1*.

Table 2 Degree of hydrolysis, *X*, and characteristic ratios of elemental analysis for homopolymers

Sample	Hydrolysis degree (mol%)	$\frac{\%\,N/14}{\%\,Cl/35.5}$	$\frac{\%\,N/14}{\%\,S/32.1}$	$\frac{\%\,Na/23}{\%\,S/32.1}$
pMADQUAT	3.35	1.02	–	–
pNaAMPS	1.33	–	1.04	1.03



Scheme 1

Table 1 Elemental analysis of homopolymers (wt%)

Sample	COO	H_2O	C	H	N	O	S	Cl	Na
pMADQUAT									
Calculated	–	–	52.05	8.67	6.75	15.42	–	17.11	–
Calculated[a]	–	6.07	48.89	8.89	6.34	19.88	–	16.07	–
Experimental[b]	0.63		49.57	9.83	5.99	19.80	–	14.81	–
pNaAMPS									
Calculated	–	–	36.68	5.24	6.11	27.95	13.97	–	10.04
Calculated[a]	–	2.36	35.81	5.38	5.97	29.39	13.64	–	9.80
Experimental[c]	0.23		37.16	6.17	5.42	30.44[d]	11.95	–	8.86

[a] Calculated results after correction for water
[b] Dialysed sample
[c] Non-dialysed sample
[d] Calculated by complement to 100% (no titration of O in the presence of Na)

Note that the neutralization between two oppositely charged monomers may be either inter- or intramolecular. In the latter case, the flexibility of the chain allows interactions to occur between units far from each other. Although the above representation is purely schematic, it takes into account all possible types of interactions. The proportions of the different species cited in *Scheme 1* were calculated from the elemental analysis of Na, Cl, S and N and by using equations (2) to (4):

$$\text{mol\% M(Cl)} = \frac{n_{\text{M(Cl)}}}{n_{\text{total}}} \tag{2}$$

$$\text{mol\% A(Na)} = \frac{n_{\text{A(Na)}}}{n_{\text{total}}} \tag{3}$$

$$\text{mol\% (AMPS–MAD)} = 2\frac{n_{\text{AMPS}}}{n_{\text{total}}} = 2\frac{n_{\text{MAD}}}{n_{\text{total}}} \tag{4}$$

where $n_{\text{total}} = n_{\text{A}} + n_{\text{M}}$. Equation (4) assumes that $n_{\text{AMPS}} = n_{\text{MAD}}$ (i.e. when a chloride ion leaves a macromolecular chain, so does a sodium ion).

In case the calculation does not lead to a perfect equality of n_{AMPS} and n_{MAD}, it is preferable to substitute the following equations for equation (4):

$$\text{mol\% (AMPS–MAD)} = 2\min\left(\frac{n_{\text{AMPS}}}{n_{\text{total}}}, \frac{n_{\text{MAD}}}{n_{\text{total}}}\right) \tag{5}$$

if $n_{\text{AMPS}} > n_{\text{MAD}}$:

$$\text{mol\% (A)} = \frac{n_{\text{AMPS}} - n_{\text{MAD}}}{n_{\text{total}}} \tag{6}$$

if $n_{\text{MAD}} > n_{\text{AMPS}}$:

$$\text{mol\% (M)} = \frac{n_{\text{MAD}} - n_{\text{AMPS}}}{n_{\text{total}}} \tag{7}$$

The (A) and (M) terms correspond to the AMPS and MADQUAT units which cannot fall in any of the other categories. In fact, equations (6) and (7) provide an estimation of the errors pertaining to the elemental analysis data. Note also that the loss of the inorganic counterions can only occur during the recovery and the purification of copolymers. This led us to evaluate the impact of dialysis on the copolymer composition.

The data reported in *Table 3* show the excellent agreement between the initial monomer compositions in the feed and the copolymer compositions determined from elemental analysis of S and N. As for the homopolymers, the degree of hydrolysis was found to be practically negligible. Moreover, the history of the sample (dialysis) does not affect the data. For most of the samples, several analyses were run with good reproducibility.

In *Table 4* are listed the molar proportions of each of the components of the copolymers calculated from equations (2) to (7). These include the moles of AMPS–MADQUAT complexes, the moles of free NaAMPS and free MADQUAT as well as those of the non-identified (A) and (M) components. The description of the copolymer species is fairly accurate since the proportion of the latter components is quite low (≃5% at most). Closer examination of *Table 4* reveals very different results depending on whether the samples were dialysed or not.

Before dialysis, the polyanions and polycations are still bound to their counterions and little mer pairing is observed. The fluctuations in the data which sometimes appear for similar samples arise from the low values determined by elemental analysis. These errors were taken into account in *Figure 1* which shows the development of the monomers' self-neutralization with the mole fraction of NaAMPS in the copolymer. As sodium chloride is quite insoluble in 2-propanol, simple copolymer precipitation followed by several washings

Table 3 Copolymer composition calculated from elemental analysis data

		Molar monomer composition in the feed		Molar copolymer composition	
Sample	Treatment[a]	NaAMPS	MADQUAT	NaAMPS	MADQUAT
A20/M80	nd	18.7	81.3	18.3	81.7
	d			18.7	81.3
A35/M65	nd (1)	32.3	67.7	35.4	64.6
	nd (2)			32.5	67.5
	d (1)			34.8	65.2
	d (2)			32.6	67.4
A50/M50	nd	47.3	52.7	48.6	51.4
	d	49.5	50.5	50.0	50.0
A60/M40	nd (1)	63.2	36.8	59.5	40.5
	nd (2)			61.0	39.0
	d (1)			62.5	37.5
	d (2)			62.2	37.8
A80/M20	nd (1)	78.6	21.4	76.6	23.4
	nd (2)			77.0	23.0
	d (1)			78.5	21.5
	d (2)			76.0	24.0

[a] nd: non-dialysed; d: dialysed; (1), (2): first and second analyses for the same sample

Table 4 Molar proportions of the different components in the copolymer series as derived from elemental analysis

Sample	Treatment[a]	AMPS-MAD (mol%)	A(Na) (mol%)	M(Cl) (mol%)	(A) (mol%)	(M) (mol%)
A20/M80	nd	12.4	6.6	75.5	5.5	–
	d	36.4	0.5	63.0	–	0.1
A35/M65	nd (1)	5.4	26.9	61.8	5.8	–
	nd (2)	12.9	26.1	60.3	–	0.7
	d (1)	63.6	3.0	31.2	–	2.2
	d (2)	65.3	0.0	33.3	–	1.4
A50/M50	nd	10.8	39.6	46.0	3.6	–
	d	96.4	0.0	1.8	1.8	–
A60/M40	nd (1)	4.9	57.0	32.2	–	5.8
	nd (2)	11.3	55.4	29.2	–	4.2
	d (1)	72.6	21.3	1.2	4.9	–
	d (2)	73.2	21.6	1.2	4.1	–
A80/M20	nd (1)	4.2	74.4	20.7	–	0.6
	nd (2)	0.0	77.0	18.3	–	4.7
	d (1)	40.0	53.4	1.5	5.1	–
	d (2)	34.1	59.0	4.5	–	2.1

[a] nd: non-dialysed; d: dialysed; (1), (2): first and second analyses for the same sample

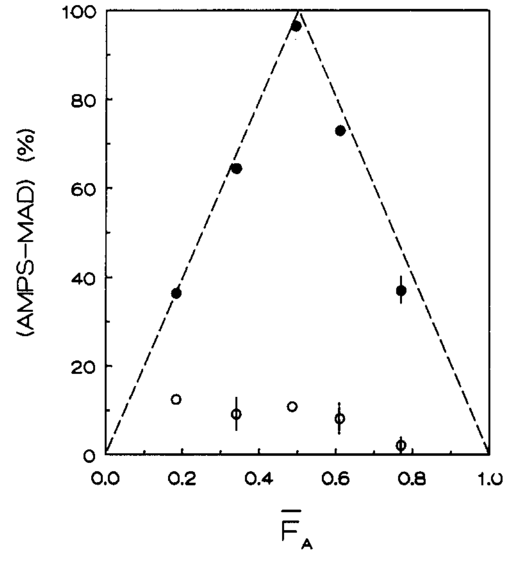


Figure 1 Variation of monomers' self-neutralization *versus* NaAMPS molar fraction: (○) non-dialysed samples; (●) dialysed samples

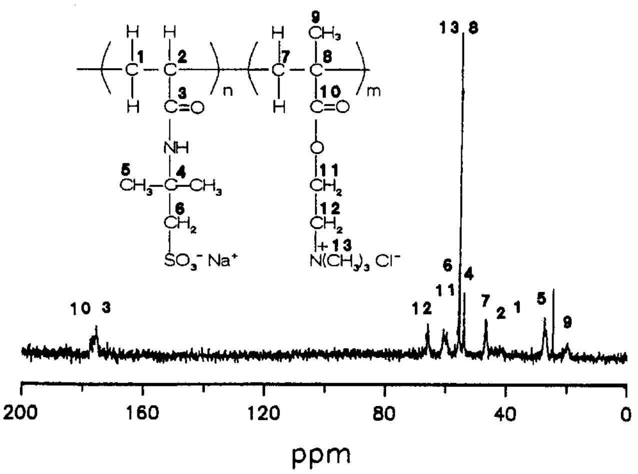


Figure 2 Typical ^{13}C n.m.r. spectrum of a copolymer

with the same solvent gives compounds in which most of the inorganic counterions initially present are to be found.

However, data after dialysis clearly show that the process allows one to efficiently remove the residual sodium chloride salt since the materials tend to self-neutralize almost completely. Under these conditions, the quantity of inorganic counterions displaced by organic counterions during mer-pairing increases as the copolymer approaches an equimolar incorporation of NaAMPS and MADQUAT (*Figure 1*). In particular, the anionic and cationic monomers of sample A50/M50 with balanced stoichiometry are completely paired, with no residual sodium or chloride counterions left in the solution. These results are comparable to those obtained by McCormick and Johnson[9] and Peiffer and Lundberg[11] on other ampholytic copolymers prepared in aqueous solution.

^{13}C n.m.r. and i.r. structural analysis. A typical ^{13}C n.m.r. spectrum of a copolymer can be seen in *Figure 2*. Under the experimental conditions selected, the signal-to-noise ratio is weak in spite of numerous scans. In general, the spectra reveal few carbonated impurities, confirming the conclusions drawn from elemental analysis.

I.r. spectra representative of pMADQUAT and of a copolymer are shown in *Figures 3* and *4*. The absorbance peaks correspond to the characteristic groups of NaAMPS and MADQUAT units.

Partial specific volume measurements

The calculation of the volume fraction of the dispersed phase of the latex formed after polymerization requires the knowledge of the partial specific volume of the

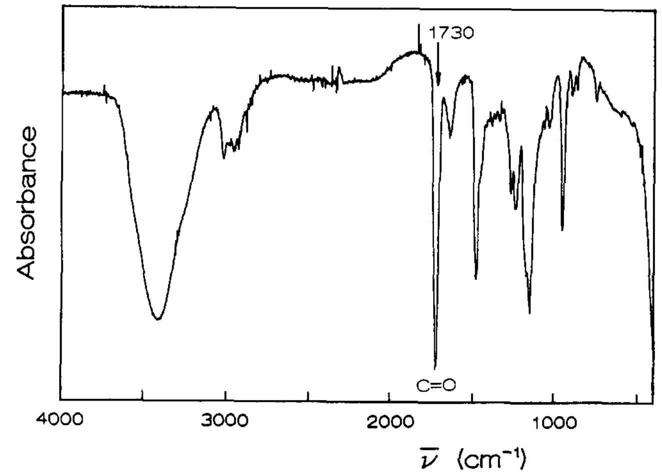


Figure 3 Typical i.r. spectrum of homo-pMADQUAT

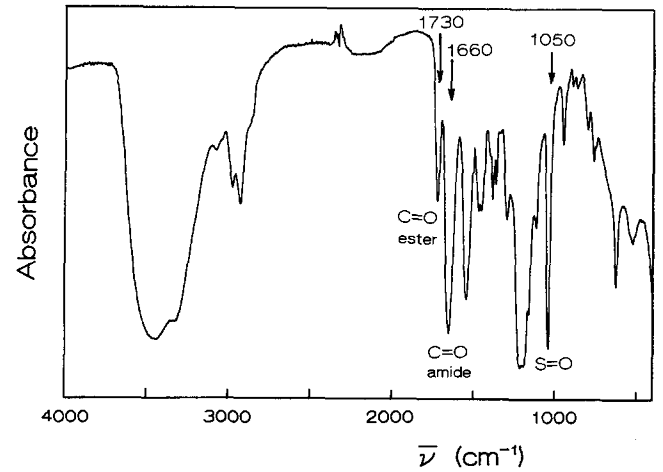


Figure 4 Typical i.r. spectrum of a copolymer (sample A80/M20)

polymer $\bar{v}_2$. The latter can be deduced from the variation of the specific volume of the solution, $\bar{v}_{12}$, with polymer concentration:

$$\bar{v}_{12} = v_1 + (\bar{v}_2 - v_1)c \tag{8}$$

where v_1 is the specific volume of the solvent. An example of the plot $\bar{v}_{12} = f(c)$ obtained for two polyampholytes is given in *Figure 5*. The different values of the polymer density ($d = 1/\bar{v}_2$) are reported in *Table 5*. The molar volume V_p was calculated from the copolymer compositions listed in *Table 3*. The plot of V_p *versus* copolymer composition is reported in *Figure 6*. The linear variation observed shows that the molar volumes of the monomeric units are, with good approximation, additive.

Molecular weight studies

The molecular weights of the copolymers were determined by static light scattering. The experimental study was complicated by the fact that the samples investigated are copolymers which are furthermore polyelectrolytes. As a result, conventional light scattering leads to an apparent molecular weight, $\bar{M}_{app}$, rather than the true average molecular weight, $\bar{M}_w$. For copolymers heterogeneous in composition, Bushuk and Benoit[20] have derived the following relationship relating these two quantities:

$$\bar{M}_{app} = \bar{M}_w + 2P\left(\frac{\nu_A - \nu_B}{\nu}\right) + Q\left(\frac{\nu_A - \nu_B}{\nu}\right)^2 \tag{9}$$

with

$$P = \frac{\sum_i M_i C_i \Delta x_i}{\sum_i C_i}$$

and

$$Q = \frac{\sum_i M_i C_i (\Delta x_i)^2}{\sum_i C_i}$$

Here, C_i is the concentration of molecules of molecular weight M_i. The quantity $\Delta x_i = x_i - x_0$ is the deviation in composition of molecules of type i from the average composition x_0. The parameters ν_A, ν_B and ν are the refractive index increments of homopolymers A and B

Table 5 Density and molar volume of the copolymer series at 25°C

Sample	d (g cm^{-3})	$V_p = \frac{\bar{M}}{d}$ (cm^3 mol^{-1})[a]
pMADQUAT	1.28_9	161.0
A20/M80	1.33_8	158.0
A50/M50	1.46_0	149.3
A80/M20	1.60_0	140.0
pNaAMPs	1.74_3	131.4

[a] $\bar{M} = x_0 M_A + (1 - x_0) M_M$ (M_A and M_M: molecular masses of NaAMPS and MADQUAT monomers, respectively)

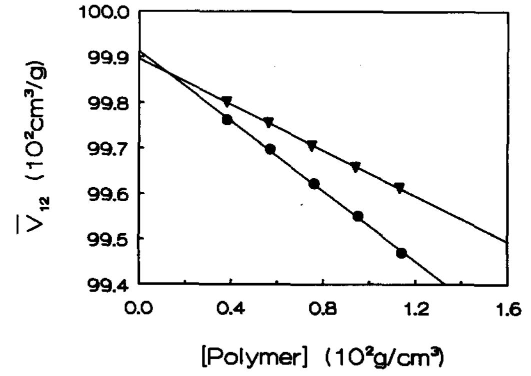


Figure 5 Variation of the specific volume of 0.1 M NaCl aqueous solutions with polymer concentration: (●) A80/M20; (▼) A20/M80

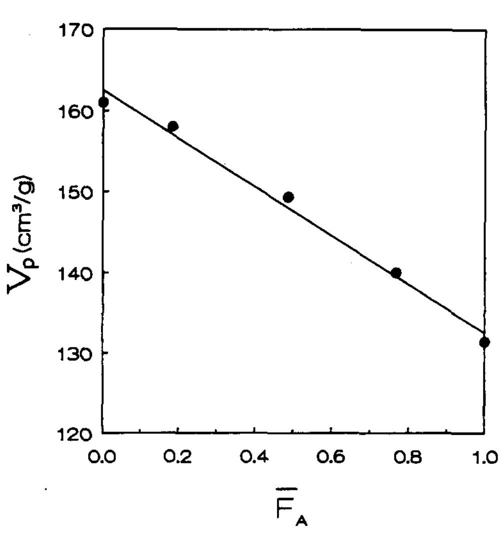


Figure 6 Variation of the copolymer molar volume with the mole fraction of NaAMPS in the copolymer (the variation is linear: $V_p = 162.5 - 30.0\bar{F}_A$ ($r = 0.995$))

Table 6 Refractive index increments for the polymer series

Sample	C_{NaCl} (mol l^{-1})	d*n*/d*C* (cm^3 g^{-1})
pMADQUAT	1.0	0.157
pNaAMPS	1.0	0.144
A80/M20	2.0	0.140
A60/M40	2.0	0.144
A50/M50	1.0	0.153
	2.0	0.145
	3.0	0.136
	4.0	0.134
A35/M65	2.0	0.146
A20/M80	2.0	0.150

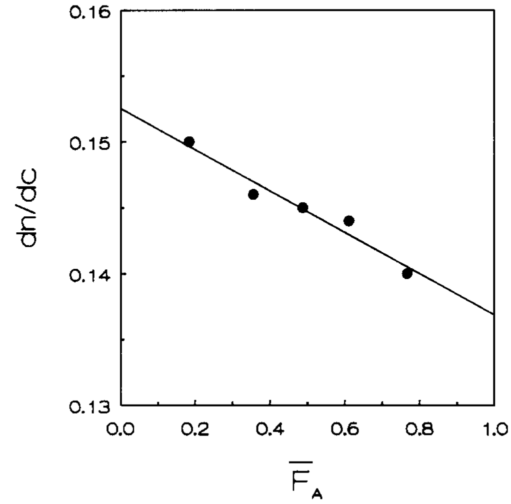


Figure 7 Variation of d*n*/d*c* with the mole fraction of NaAMPS in the copolymer (2.0 M NaCl; the variation is linear: d*n*/d*c* = $0.016\bar{F}_A + 0.152$ ($r = 0.980$))

and of the copolymer in the solvent considered, respectively.

Equation (9) was established by assuming the additivity of the refractive index increments of the components:

$$\nu = \frac{dn}{dc} = x_0\nu_A + (1 - x_0)\nu_B \qquad (10)$$

Table 6 reports the values of the refractive index increments measured for copolymers of various compositions in NaCl aqueous solutions. The variation of d*n*/d*c* with NaAMPS content in the feed is linear (*Figure 7*), thus allowing the use of equation (9) for the $\bar{M}_w$ determination.

As an example, we obtain for sample A50/M50 in 1.0 M NaCl aqueous solution:

$$\bar{M}_{app} = \bar{M}_w + 0.170P + 0.007Q$$

As will be shown in the next section, the monomer sequence distribution is not far from that observed for random copolymerization. It follows that Δx_i should be small in every case and therefore low values for P and Q are expected. Furthermore, the quantity $(\nu_A - \nu_B)/\nu$ is also small as seen from the d*n*/d*c* values reported in *Table 6*. The molecular-weight values measured by light scattering should then be located in the bottom area of the well known parabola $\bar{M}_{app} = f((\nu_A - \nu_B)/\nu)$, (see ref. 20), so that $\bar{M}_{app} \simeq \bar{M}_w$. In the following, we have considered that this equality was valid for the whole copolymer series.

A second difficulty comes from the electrolytic nature of the copolymer. To suppress the polyelectrolyte effect, the LS experiments were performed in NaCl aqueous solutions. It should be noted that for a rigorous analysis of LS data, the refractive index increment should be measured after the establishment of the osmotic equilibrium between polyelectrolyte solution and solvent. Such a refinement was not taken into account in the present study. However, the error remains limited because the ions of the salt added in the solvent are identical to the counterions of the polyelectrolyte. Experimental data at various salt concentrations (see below) support this argument. Furthermore, in the range of $\bar{M}_w$ investigated, experimental errors are undoubtedly larger than the errors introduced by neglecting the multicomponent nature of the solvent.

Weight-average molecular weights, $\bar{M}_w$, radii of gyration $\langle R_G^2 \rangle^{1/2}$ and second virial coefficients, A_2, as determined in NaCl aqueous solutions are listed for the high-conversion copolymer series in *Table 7*. An example of a Zimm plot is given in *Figure 8*. In order to account for the curvature which sometimes appears on the Zimm plots for these high-molecular-weight values ($qR_G > 1$), the plot of the scattered intensity, I, at a given concentration was adjusted by a second-order regression[21]. The variation of I at a given angle was fitted by a least-squares method.

The values reported in *Table 7* suffer from a high degree of uncertainty since, because of the high molecular weights involved, the measurements are carried out at

Table 7 Average molecular weights, radii of gyration and second virial coefficients for the homopolymers (1.0 M NaCl) and the copolymers (2.0 M NaCl)

Sample	$\bar{M}_w$ ($\times 10^{-6}$)	$\langle R_G^2 \rangle^{1/2}$ (Å)	A_2 ($\times 10^4$) (cm^3 g^{-1})
pMADQUAT	13.1 ± 1.5	2110 ± 334	−0.28 ± 1.07
pNaAMPS	8.3 ± 1.0	2280 ± 204	0.25 ± 0.86
A80/M20	11.6 ± 1.3	1970 ± 229	−5.90 ± 1.04
A60/M40	16.6 ± 4.3	2840 ± 357	1.24 ± 1.80
A60/M40^a	15.4 ± 2.1	2820 ± 207	1.93 ± 1.51
A50/M50	14.1 ± 1.3	2440 ± 207	−0.58 ± 1.37
A50/M50^a	15.2 ± 3.5	2330 ± 363	−2.28 ± 2.00
A35/M65	11.8 ± 1.7	2410 ± 121	2.75 ± 4.48
A20/M80	12.1 ± 1.9	2200 ± 161	0.36 ± 1.58

^{a}Dialysed sample

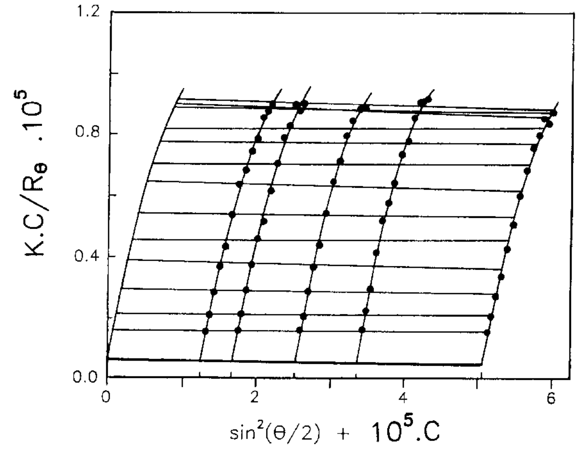


Figure 8 Zimm plot for sample A50/M50 (1.0 M NaCl)

the limit of the Guinier approximation. Nevertheless, the following conclusions can be made:

(i) The inverse microemulsion polymerization process leads to ultra-high molecular masses ($\geqslant 10^7$).

(ii) The variation of the molecular weight with copolymer composition is limited (*Figure 9*).

(iii) The values of the second virial coefficients are close to zero; thus the aqueous salt solution behaves as a θ-solvent for both homopolymers and copolymers.

(iv) Dialysis does not affect the data.

Effect of concentration and nature of the salt. It is well recognized that copolymers containing a high charge density of anionic and cationic groups exhibit strong electrostatic interactions. When the charge screening by a salt is not sufficient, one expects the formation of some aggregates held in the solution via intermolecular forces.

In order to check this possibility, we have performed some LS experiments on sample A50/M50 at various NaCl contents ranging from 1.0 to 4.0 M. The results are listed in *Table 8*. No significant variation of $\bar{M}_w$ is observed, leading to the conclusion that aggregates are probably absent in the salt solutions whatever the salt content.

Furthermore, above the critical salt concentration needed to ensure the chains' solubilization ($\simeq 0.9$ M for sample A50/M50), the solvent quality is unaffected upon further addition of salt, as attested by the almost constant A_2 values. These results were further confirmed by SANS experiments[14]. In the same reference, it was also shown that the nature of the salt affects the copolymer aqueous solution properties. We found here that the type of salt used does not affect the characteristics of the samples. Thus, an LS experiment carried out on sample A50/M50 after dialysis (i.e. inorganic counterions-free) in 0.6 M NaI aqueous solution ($dn/dc = 0.161$ cm^3 g^{-1}) led to the following data:

$$M_w = (13.2 \pm 2.2) \times 10^6$$

$$\langle R_G^2 \rangle^{1/2} = 2150 \pm 155 \text{ Å}$$

$$A_2 = -1.53 \times 10^{-4} \pm 2.06 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1}$$

which are quite comparable to those measured in NaCl aqueous solutions.

Effect of the initial microemulsion composition. In part I of this series[13], we have shown that the size of the microlatex particles formed after microemulsion polymerization increases upon increasing the monomer over surfactant concentrations in the initial microemulsion. *Table 9* shows that the molecular weight variation follows the same trend.

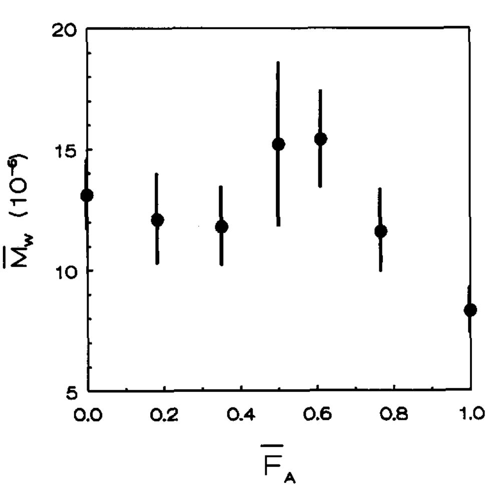


Figure 9 Variation of polymer molecular weight with the mole fraction of NaAMPS in the copolymer

Table 8 Characteristics of sample A50/M50 in various NaCl aqueous solutions

C_{NaCl} (mol l^{-1})	$\bar{M}_w$ ($\times 10^{-6}$)	$\langle R_G^2 \rangle^{1/2}$ (Å)	A_2 ($\times 10^4$) (cm^3 g^{-1})
1.0	15.7±2.1	2920±113	−1.70±1.41
1.5	16.5±2.8	2510±297	−1.42±0.87
2.0	15.2±3.5	2330±363	−2.22±2.00
3.0	14.0±2.1	2870±202	−1.64±2.92
4.0	16.5±2.4	3020±382	−1.76±1.64

Table 9 Variation of the molecular weights, radii of gyration and second virial coefficients with the monomer/surfactant ratio

Sample	Monomer/ Surfactant (w/w)	$\bar{M}_w$ ($\times 10^{-6}$)	$\langle R_G^2 \rangle^{1/2}$ (Å)	A_2 ($\times 10^4$) (cm^3 g^{-1})
A60/M40	1.86	15.4±2.1	2820±207	1.93±1.51
	0.99	8.8±1.6	2280±315	4.32±1.61
A50/M50	1.80	15.2±3.5	3440±363	−2.22±2.00
	1.00	8.6±1.3	2090±154	−2.23±1.57

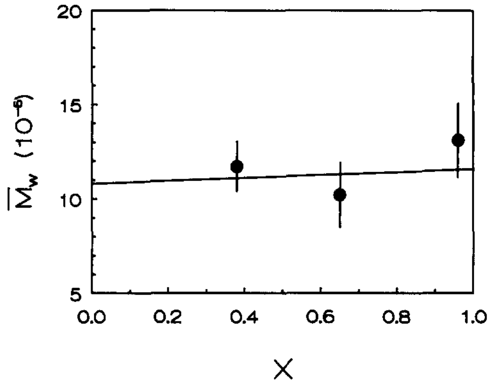


Figure 10 Variation of pMADQUAT molecular weight with degree of conversion

Development of molecular weight with conversion. Figure 10 shows the development of the molecular weight of MADQUAT homopolymer as a function of the degree of conversion, X. The molecular weight of the polymer is almost independent of the degree of conversion, as expected for a free-radical polymerization mechanism and in agreement with acrylamide[22] and acrylamide–sodium acrylate[23] microemulsion polymerizations. It should be noted that owing to the very fast rate of reaction (a few minutes[13]), successive samples could not be taken during the same experiment. Thus, each copolymer corresponds to a separate experiment. This is good evidence of the reproducibility of the experiments.

Copolymer microstructure: reactivity ratios studies

In this study we are interested in the characterization of the microstructure of NaAMPS–MADQUAT copolymers prepared in microemulsion and in the determination of their reactivity ratios for comparison with those from solution polymerization.

Table 10 Feed compositions (f_A), copolymer compositions ($\bar{F}_A$) and degree of conversion (X)

Reaction medium	f_A	$\bar{F}_A$	X (%)
Microemulsion	0.185	0.109	10.0
	0.280	0.192	2.4
	0.330	0.200	10.0
	0.500	0.379	12.6
	0.677	0.599	4.0
	0.782	0.698	8.8
	0.890	0.865	7.9
Solution	0.182	0.230	23.9
	0.181	0.214	18.7
	0.198	0.202	21.5
	0.248	0.241	20.7
	0.248	0.258	19.0
	0.349	0.315	13.2
	0.651	0.483	21.1
	0.651	0.490	11.4
	0.749	0.523	20.3
	0.846	0.563	15.8
	0.846	0.571	7.7

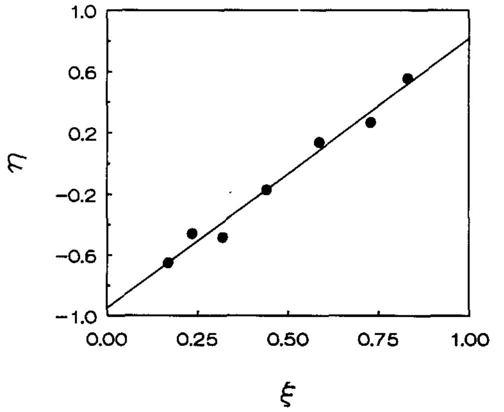


Figure 11 Kelen-Tüdos plot for the determination of reactivity ratios for the microemulsion copolymerization of NaAMPS with MADQUAT (α, η and ξ are defined in ref. 25; $\alpha = 2.074$)

The compositions of the copolymers prepared in microemulsion and in solution were determined from the elemental analysis of S and N (equation (1) and *Table 10*).

Reactivity ratios for copolymers prepared in microemulsions. Reactivity ratios were calculated by elemental analysis from monomer feed and low-conversion–compositional data (<10%, see *Table 10*). Three methods were employed: the linear methods of Fineman–Ross[24] and Kelen–Tüdos[25] (*Figure 11*) and the non-linear least-squares Tidwell–Mortimer methods[26,27]. These methods are based on the well known Mayo–Lewis[28] equation:

$$F_A = \frac{(r_A - 1)f_A^2 + f_A}{(r_A + r_M - 2)f_A^2 + 2(1 - r_M)f_A + r_M} \qquad (10)$$

with $F_A = d[A]/(d[A] + d[M])$: instantaneous molar fraction of monomer A in the copolymer, and $f_A = [A]/([A] + [M])$: instantaneous mole fraction of monomer A in the feed.

Equation (10) relates instantaneous values. Its solution is only strictly applicable to copolymerizations carried out to very low conversions where the average copolymer composition and the instantaneous composition correspond closely.

These methods were initially derived for polymerization in homogeneous solutions but they can also be applied here because almost all of the monomers are located within the aqueous domains of the microemulsions. This confinement arises from the type of monomers (exclusively water-soluble) as well as from the experimental conditions used in the process which allows one to neglect corrections for monomer partitioning between the oil and the water phases. An excellent agreement is observed between the different sets of values of the reactivity ratios obtained by the three methods (*Table 11*). In particular, although the Fineman–Ross equation is not symmetrical with respect to the definition of which monomer is A and which is M, its representation leads to two similar sets of values for r_A and r_M.

Figure 12 shows the monomer incorporation curve derived from the Mayo–Lewis equation (with $r_A = 0.81$ and $r_M = 1.97$) in which mole percent NaAMPS in the copolymer is plotted *versus* mole percent of NaAMPS in the feed (solid line). The first diagonal corresponding to the case where both r_A and r_M are unity (random copolymerization) is given for reference.

Reactivity ratios for copolymers prepared in fresh water. As seen in *Table 10*, the number of low-conversion samples obtained in homogeneous aqueous solution is limited. Therefore, the reactivity ratios were calculated by using the modified version of the Kelen–Tüdos

Table 11 Reactivity ratios of NaAMPS (r_A) and MADQUAT (r_M) in microemulsion polymerization

Method	r_A	r_M
Fineman–Ross 1 = NaAMPS 2 = MADQUAT	0.84	2.04
Fineman–Ross 1 = MADQUAT 2 = NaAMPS	0.79	1.93
Kelen–Tüdos	0.81	1.97
Tidwell–Mortimer	0.81	1.97

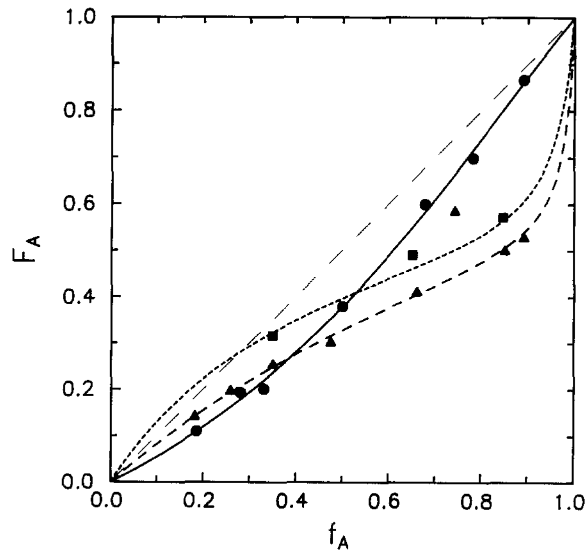


Figure 12 Incorporation curves for NaAMPS and MADQUAT monomers (the experimental points correspond to low-conversion samples (X < 13%)): (●, —) in microemulsion; (■, ···) in aqueous solution; (▲, – – –) in 2 M NaCl aqueous solution

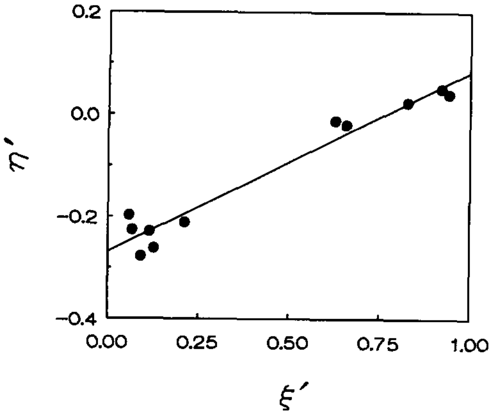


Figure 13 Kelen-Tüdos plot for the determination of reactivity ratios for the aqueous solution copolymerization of NaAMPS with MADQUAT (α', η', ξ' are defined in ref. 29; $\alpha'=2.375$)

method[29] which includes the degree of conversion (*Figure 13*). A graphical evaluation yields reactivity ratios of $r_A=0.08$ and $r_M=0.64$ for the monomer pair. The corresponding incorporation curve reported in *Figure 12* shows an azeotropic copolymer composition for $f_A^0=0.28$.

Validity of the results. The Mayo–Lewis equation fails to describe adequately the instantaneous monomer incorporation in the copolymer in a number of cases including penultimate effects, depropagation or intramolecular interactions. The results reported in this paper show that monomer associations form via mer-pairing. In order to check whether the Mayo–Lewis equation can be applied to the present case, we have studied the drift in copolymer composition with conversion by numerical integration of the Mayo–Lewis equation using the equations derived by Skeist[30] and Meyer and Lowry[31]. For this purpose two series of copolymers of given composition were prepared at variable degrees of conversion by polymerization in microemulsion and in homogeneous aqueous solution (salt-free).

The average copolymer composition–conversion data obtained from each series are reported in *Figures 14* and *15*. The good agreement between experimental data (●, ○, symbols) and calculated curves (solid lines) suggests that the Mayo–Lewis equation describes adequately the kinetic processes occurring in the copolymerization reaction and, therefore, allows a proper determination of the reactivity ratios.

Influence of the method of preparation on copolymer microstructure. It is evident from the above results that the reactivity ratios of NaAMPS and MADQUAT are significantly affected by the method of synthesis: in microemulsion, $r_A=0.81$ and $r_M=1.97$; in aqueous solution, $r_A=0.08$ and $r_M=0.64$.

The 95% confidence regions depicted in *Figure 16* by using the Tidwell–Mortimer non-linear regression show no possible overlapping between the reactivity-ratio values obtained in microemulsion and in solution. The differences observed between the two sets of values must therefore reflect some specific physical and/or chemical processes.

The values of the product r_Ar_M suggest a very different microstructure for the copolymers prepared in microemulsion and in solution. In the former case, r_Ar_M is slightly higher than unity ($\simeq 1.6$). The copolymers show a tendency to form poly-A and poly-M sequences which are longer than those in a random copolymer of the same chemical composition ($r_Ar_M=1$). The statistical distribution of monomer sequences (A–A), (M–M) and (A–M) was calculated, according to Igarashi[32], using experimental reactivity ratios. The calculation of mean sequence lengths, μ_A and μ_M, was also performed

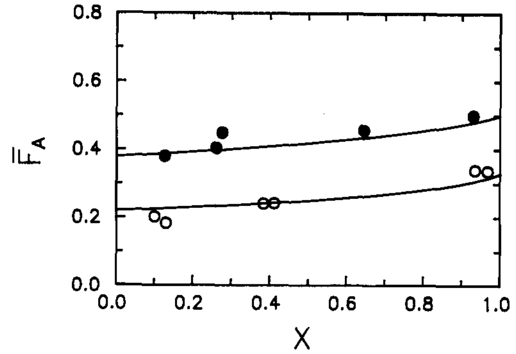


Figure 14 Variation of average copolymer composition with degree of conversion X, for two series prepared in microemulsions: (○) $f_A^0=0.33$; (●) $f_A^0=0.50$; (——) calculated curves with $r_A=0.81$ and $r_M=1.97$

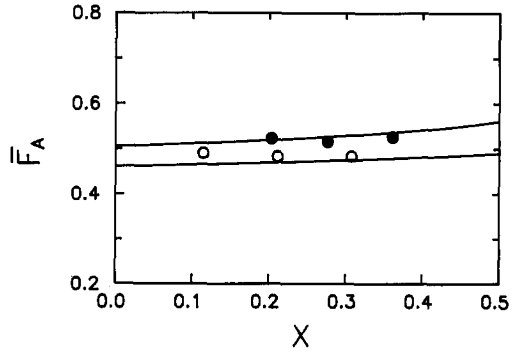


Figure 15 Variation of $\bar{F}_A$ with X for two series prepared in aqueous solution: (○) $f_A^0=0.65$; (●) $f_A^0=0.75$; (——) calculated curves with $r_A=0.08$ and $r_M=0.64$

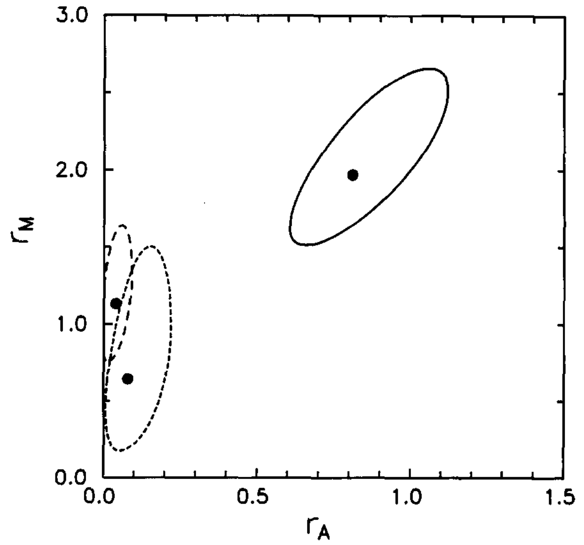


Figure 16 95% Confidence regions for the NaAMPS-MADQUAT reactivity ratios obtained in microemulsion (——), in aqueous solution (- - -) and in 2 M NaCl aqueous solution (– – –) (estimate made on low-conversion samples ($X<15\%$))

according to the method of Pyun[33]. The simulation of the copolymer microstructure deduced from these statistical data (see *Figures 17* and *18*) reveals a monomer-sequence distribution quite close to that observed for a copolymer obeying Bernoullian statistics ($r_A = r_B = 1$, dotted lines in *Figures 17* and *18*).

For copolymers prepared in aqueous solution, $r_A r_M$ is close to zero ($\simeq 0.05$). The macromolecules present a large number of sequences in which the NaAMPS and MADQUAT units alternate. Note also that the drift in copolymer composition with the degree of conversion is strongly influenced by the method of preparation. This drift can become particularly significant in the case of solution polymerization, when the composition in the monomer feed deviates from the azeotropic value ($f^0_A = 0.28$). Thus, for a stoichiometric proportion of the monomers, a high-conversion sample ($X \simeq 0.99$) will consist of a mixture of a NaAMPS homopolymer and of a practically alternated NaAMPS–MADQUAT copolymer (*Figure 19*). The more pronounced the effect, the larger the deviation from the azeotropic composition. On the contrary, the high-conversion samples obtained in microemulsions are much more homogeneous in composition (*Figure 20*). In particular, a MADQUAT monomer, in spite of a faster incorporation than NaAMPS, will never be totally consumed before a quantitative yield is reached.

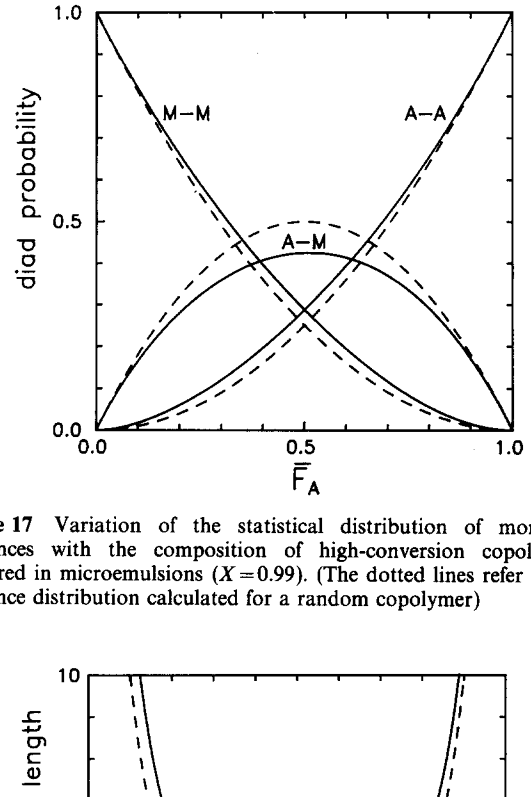


Figure 17 Variation of the statistical distribution of monomer sequences with the composition of high-conversion copolymers prepared in microemulsions ($X = 0.99$). (The dotted lines refer to the sequence distribution calculated for a random copolymer)

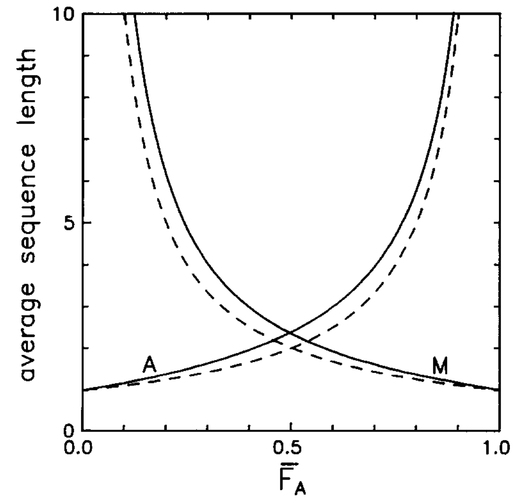


Figure 18 Variation of the average sequence lengths with the composition of copolymers prepared in microemulsions ($X = 0.99$). (The dotted lines refer to those calculated for a random copolymer)

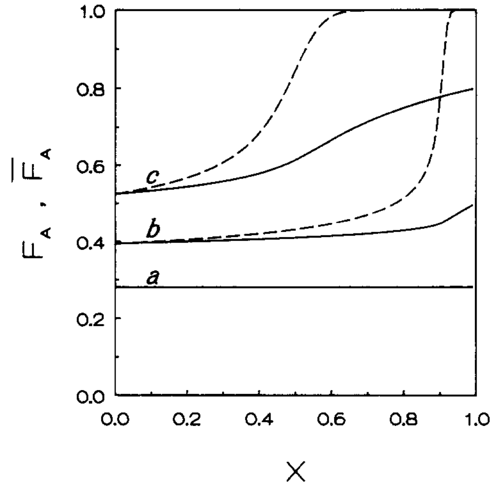


Figure 19 Aqueous solution polymerization. Simulation of the variation of the copolymer composition with the degree of conversion: (——) $\bar{F}_A$; (– – –) F_A; (a) $f^0_A = 0.28$; (b) $f^0_A = 0.50$; (c) $f^0_A = 0.80$

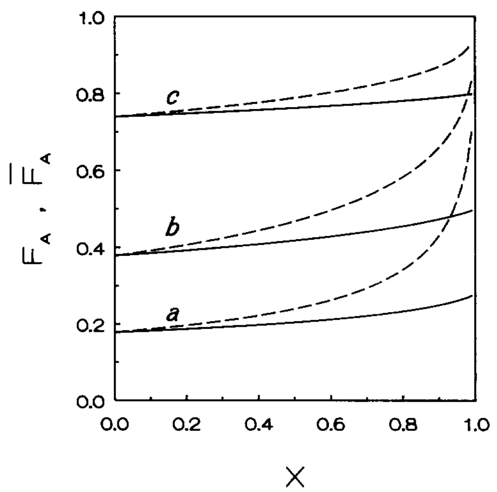


Figure 20 Microemulsion polymerization. Simulation of the variation of the copolymer composition with the degree of conversion: (——) $\bar{F}_A$; (– – –) F_A; (a) $f^0_A = 0.28$; (b) $f^0_A = 0.50$; (c) $f^0_A = 0.80$

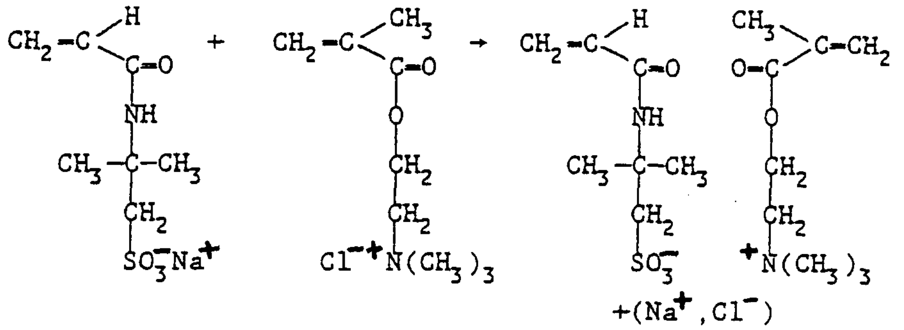
DISCUSSION

The above results are in line with recent studies of Candau *et al.*[19] and Kozakiewicz and Lipp[34] who have shown that the reactivity-ratio values of various pairs of water-soluble monomers are affected by the method of preparation, especially when the monomer(s) involved is polar. As seen in *Table 12*, the reactivity ratios of monomer pairs depend upon whether the polymerization reaction medium is a homogeneous solution, emulsion or microemulsion. More precisely, the values found in solution and in emulsion correspond closely but differ strongly from those in microemulsion. An interesting finding is that microemulsion polymerization seems to improve the structural homogeneity of the copolymers since in all the cases investigated, the reactivity-ratio values tend towards unity. In this respect, the case of

Table 12 Reactivity-ratio values for some monomer pairs

	Aqueous solution		Emulsion		Microemulsion	
Monomer pair	r_A	r_B	r_A	r_B	r_A	r_B
Acrylamide (A)+ Sodium acrylate (B) (pH=9)	0.95[a]	0.30[a]	1.06[a]	0.29[b]	0.95±0.15[c]	0.89±0.15[c]
Acrylamide (A)+ MADQUAT (B)	0.25[d] 0.43±0.18[e]	1.71[d] 2.39±0.38[e]	Values close to those in solution[e]		0.74[f]	1.23[f]

[a] Ref. 35
[b] Ref. 36
[c] Ref. 19
[d] Ref. 37
[e] Ref. 38
[f] Ref. 34



Scheme 2

poly(acrylamide-*co*-sodium acrylate)s is particularly remarkable. A careful ^{13}C n.m.r. study has shown that the monomer-sequence distribution is perfectly random since it obeys Bernoullian statistics with both reactivity ratios close to unity. The average copolymer composition was also found to be independent of the degree of conversion[19]. In the case of polyampholytes formed by copolymerization in solution, it was shown in this paper that the monomer-sequence distribution is close to alternation whilst it is almost random for samples prepared in microemulsions.

Before discussing the values of the reactivity ratios found for the monomer pair in solution and in microemulsion, we think it is useful to calculate r_A and r_M on the basis of the *Q,e* scheme[39]. For this purpose, we have used the values reported in the literature for the aqueous solution copolymerization of acrylamide (AM) with NaAMPS[40] ($r_A=0.52$, $r_{AM}=1.00$) on one hand and with MADQUAT[37] ($r_M=1.71$, $r_{AM}=0.25$) on the other.

The *Q,e* scheme using *Q,e* values of 1.12 and 1.19 for acrylamide, respectively[41], provides the following values for the copolymerization of NaAMPS and MADQUAT in aqueous solution: $r_A=0.28$, $r_M=3.57$.

The copolymerization reaction is ideal ($r_A r_M \simeq 1$). In this respect, it should be remembered that one has to be cautious when comparing theoretical values and experimental data. The intrinsic *Q,e* parameters are semiquantitative and can only provide the order-of-magnitude of the reactivity ratios.

The following statements can, however, be outlined:

(i) The reactivity of MADQUAT in solution is strongly diminished (experimental value $r_M=0.64$; theoretical value, $r_M=3.57$).

(ii) The monomer-sequence distribution experimentally found in solution is close to alternation ($r_A r_M=0.05$).

In spite of the limitations of the *Q,e* scheme, the differences observed should be characteristic of the particular behaviour of the NaAMPS–MADQUAT monomer pair copolymerized in aqueous solution. Note that under similar experimental conditions and with monomers of comparable structure, McCormick *et al.*[9,42] and Salamone *et al.*[12,16] have also obtained alternated copolymers. In addition, a recent paper by Huglin and Rego[43] has clearly shown that, in the case of the copolymerization of two charged monomers, the prediction based on the *Q,e* scheme can lead to an order-of-reactivity entirely opposite to the true experimental one. In all the cases, it appears that the intrinsic chemical reactivity of the monomers (as predicted by the *Q,e* scheme) is enormously influenced when the two monomers can interact via strong electrostatic forces. In an attempt to interpret this fact, let us assume that the monomers form associations according to *Scheme 2*.

The production of copolymers showing a strong trend to alternation, as observed in aqueous solution, suggests that these pairs are effectively present. On the contrary, for the microemulsion copolymerization, the experimental values tend to be closer to those predicted by the *Q,e* scheme. It follows that the coulombic attractions between monomers should be strongly diminished. This could be due to the high local monomer concentration in a microemulsion (3–5 M) compared to that in solution (≃0.5 M) which should produce an increased screening of the polyions by the small ions in the solution. This possibility was previously envisaged by one of us to account for the acrylamide–sodium acrylate data

Table 13 Feed compositions (f_A), copolymer compositions ($\bar{F}_A$) and degree of conversion (X) for samples prepared in 2 M NaCl aqueous solution

f_A	$\bar{F}_A$	X (%)
0.181	0.140	9.3
0.258	0.195	10.3
0.350	0.251	7.4
0.350	0.237	14.3
0.475	0.300	10.5
0.475	0.306	13.5
0.660	0.389	12.7
0.660	0.409	3.0
0.660	0.372	5.5
0.660	0.388	12.9
0.742	0.583	10.4
0.851	0.498	10.9
0.892	0.526	4.8
0.892	0.495	9.0

obtained in microemulsion polymerization[19]. Additional support was also recently provided by McCormick and Salazar[44] who reported slightly different reactivity ratios for the acrylamide and sodium 3-acrylamide-2-methylbutanoate (AM–NaAMB) monomer pair in deionized water ($r_1 = 1.23$, $r_2 = 0.50$) and in 1 M NaCl ($r_1 = 1.00$, $r_2 = 0.64$). This difference was also attributed to a decrease in electrostatic repulsion between the macroradical and unreacted NaAMB.

In order to check the above possibility, we have performed copolymerization reactions of NaAMPS and MADQUAT in 2 M NaCl aqueous solutions (*Table 13*, *Figure 12*). The reactivity-ratio values calculated by using the same procedures as in the microemulsion case led to $r_A = 0.04$, $r_M = 1.13$ (Kelen–Tüdos) and $r_A = 0.03$, $r_M = 1.12$ (Tidwell–Mortimer).

These values are not far from those obtained in pure water and therefore still deviate considerably from the microemulsion data, as shown in the 95% confidence regions reported in *Figure 16*. Other things being equal, it follows that the microenvironment alone cannot explain the more random structure observed in microemulsion polymerization. We are then forced to attribute this effect to the difference in mechanism. Exactly which factor leads to the difference in reactivity ratios remains unclear. Reactivity ratios close to one indicate that, at any time, a growing chain does not show any preference for either one of the monomers. A mechanism based on interparticular collisions followed by complete mixing of the particle content accounts fairly well for the data[19].

However, this explanation may be too simplistic, since some deviations from unity are observed as in the present case. Various causes may be at the origin of these deviations. Some partial monomer diffusion through the organic phase could favour the reactivity of one monomer with respect to the other, because of different solubilities. Also, some local monomer-concentration variations can occur, for example in the neighbourhood of the interface, owing to salting-out and cosurfactant effects of different amplitudes. In this respect, it was shown in part I of this series[13] that the electrolyte monomers produced a strong salting-out effect of the ethoxylated surfactants. Interestingly enough, the effect was more pronounced for MADQUAT. This would result in some preferential sequences of MADQUAT along the copolymer backbone, as was indeed observed.

Special mention should be made of the bootstrap model developed by Harwood[45], in which partitioning of monomers between solvent and growing polymer radicals leads to apparent reactivity ratios. In this model, Harwood warned of microstructural differences arbitrarily derived from apparent reactivity ratios and stressed the importance of direct measurement of sequence distribution. A direct ^{13}C n.m.r. analysis of the polyampholyte microstructure was beyond the scope of the present study, due to the complexity of the NaAMPS–MADQUAT pair investigated for which no data are available in the literature. However, and as mentioned above, a ^{13}C n.m.r. study of poly(acrylamide-*co*-sodium acrylate)s prepared in microemulsions gave clear evidence of a microstructure conforming to Bernoullian statistics[19]. As a consequence, it seems legitimate to infer that the reactivity ratios measured in the present study give a reliable picture of the distribution. It should also be noted that the copolymerization systems used in the Harwood model are monomer pairs whose solubilities differ markedly in the solvent investigated (as for example styrene–acrylamide in benzene), resulting in the preferential solvation phenomenon observed. As already emphasized, NaAMPS and MADQUAT are exclusively water-soluble, so that the bootstrap effect might not be relevant here.

The difference in mechanism should also come into play when comparing the inverse emulsion and microemulsion data of *Table 12*. In the inverse emulsions, monomer diffusion from source droplets to the polymerization locus is thought to be an important step. Their concentrations at the polymerization locus might thus be different from those in the source droplets. Reactivity ratios obtained by using the droplet concentrations as those of reacting monomers could be apparent rather than true reactivity ratios. In the inverse microemulsions, where a mechanism based on a collision process between nucleated and un-nucleated particles was proposed, the monomer proportions at the reaction sites should be maintained throughout the polymerization at their initial values, thus generating a homogeneous microstructure[19].

The above results deserve further study to fully elucidate the mechanism involved in these systems. If these were confirmed for other monomer pairs, microemulsion polymerization could become an appealing method for producing copolymers of homogeneous composition.

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