Characterization of Cationic Water-Soluble Polyacrylamides

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SYNOPSIS

Copolymers of poly(acrylamide-co-acryloyloxyethyltrimethylammonium chloride or AM–CMA) and poly(acrylamide-co-methacryloyloxyethyltrimethylammonium chloride or AM–CMM) prepared by inverse emulsion polymerization were characterized by different analytical techniques. The chemical composition of the copolymers was estimated by elemental analysis and by nuclear magnetic resonance spectroscopy (NMR). NMR spectroscopy and computer simulation were further used for investigating the polymers' sequence distribution. The poly(AM–CMA) copolymers are chemically more homogeneous than are the poly(AM–CMM). The configurational propagation of dyads and triads for the homopolymers obeys Bernouilli's statistics. For the copolymers, the chemical sequences distribution is governed by Markov's first-order statistics.

INTRODUCTION

Cationic polyelectrolytes are extensively used in the field of water treatment by flocculation of industrial sludges. One class of such high molecular weight polymers obtained through radical copolymerization of acrylamide with salified or quaternized dimethylaminoethylacrylate shows remarkable applicative properties. However, the literature dealing with the chemical characterization and the microstructural investigation of such polymers is limited. We report in this work analytical results concerning the chemical composition and the sequence distribution of the poly(acrylamide-co-acryloyloxyethyltrimethylammonium chloride) and poly(acrylamide-co-methacryloyloxyethyltrimethylammonium chloride), as well as of the corresponding homopolymers.
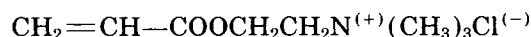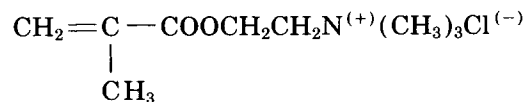
EXPERIMENTAL

Monomers

- Acrylamide (AM)
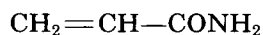
$$CH_2 = CH - CONH_2$$

- Acryloyloxyethyltrimethylammonium chloride (CMA)

$$CH_2 = CH - COOCH_2CH_2N^{(+)}(CH_3)_3Cl^{(-)}$$

- Methacryloyloxyethyltrimethylammonium chloride (CMM)

$$CH_2 = C - COOCH_2CH_2N^{(+)}(CH_3)_3Cl^{(-)}$$
$$| $$
$$CH_3$$

Solid AM (from American Cyanamid) was used without any further purification. CMA and CMM (from Orkem) were obtained by quaternizing, respectively, dimethylaminoethyl acrylate (DAMEA) and the corresponding methacrylate (DAMEMA) with methyl chloride.

Homopolymers

The reference homopolymers of AM, CMA, or CMM were obtained by radical polymerization in water under the following conditions: 1.5 mol/L of AM, CMA, or CMM, initiated by 0.03 mol/L of 2,2'-azo-bis-(2-amidinopropane)-dihydrochloride at 65°C and pH 3.5 during 4 h.

Table I   Analytical Data on Dry CMA 15, CMA 30, CMM 15, and CMM 30 Samples

Determination of (meq/g)	CMA 15	CMA 30	CMM 15	CMM 30
Nitrogen	10.85	8.85	10.75	8.55
Carboxylic groups	0.02	0.03	0.03	0.02
Amino groups	0	0	0	0
Chlorides	1.75	2.83	1.64	2.67

Copolymers

Poly(AM-co-CMA) and poly(AM-co-CMM) co-polymers having a cationic monomer molar content of, respectively, 5, 15, and 30% were obtained by an inverse emulsion polymerization technique.[1,2] For convenience, they are designated in this paper by CMA 5, CMA 15, CMA 30, CMM 5, CMM 15, and CMM 30 according to their cationic monomer content.

Analytical Methods

All the analyses were performed on CMA 15, CMA 30, CMM 15, and CMM 30 samples. Nitrogen was determined by Kjeldhal analysis, and chlorides were titrated with silver nitrate. Carboxylic groups and free amines arising from the hydrolysis of the amide or ester functions were determined by potentiometry. Active matter was determined by gravimetry after drying the samples to constant weight at 120°C. Water was determined by Karl Fischer titration.

The polymerization reactions were conducted to a high conversion degree. The residual monomer content is below 0.5% and was titrated by high-performance liquid chromatography.

^{1}H-NMR spectra were obtained from 2 wt % polymer solutions in D_2O containing 5 wt % NaCl. The spectra were recorded at 25°C using 5 mm inner diameter tubes and containing trimethylsilyl-3-propionic acid D_4-2,2,3,3:sodium salt (TSPD4) as the internal standard ($\delta = 0$ ppm). The apparatus we used was a spectrometer Cameca 350 (350 MHz ^{1}H, pulse angle 20°, acquisition time 2 s, interval between pulses 0.5 s, 500 accumulations).

The ^{13}C-NMR spectra were obtained at 25 or 40°C on 15 wt % polymer solutions using 10 mm inner diameter tubes. p-Dioxane was the internal standard ($\delta = 67.4$ ppm). The spectrometer used was a Bruker model AC 200 (50 MHz ^{13}C, pulse angle 80°, acquisition time 2 s, interval between pulses 10 s, 14,000 accumulations, ^{1}H decoupling).

RESULTS AND DISCUSSION

Experimental Results

All the analytical results on dry samples are summarized in Table I.

Characterization of the Copolymers' Sequence Distribution by Computer Simulation

During copolymerization, the chemical composition of the polymer and the distribution of monomeric sequences are governed by the reactivity ratios $r1$ and $r2$ of the monomers. According to these ratios, the chemical composition of the resulting polymers are more or less homogeneous. The distribution of the monomeric sequences can be measured either by statistical calculation or experimentally through NMR analysis of the polymers.[3,4] In this work, both methods were used for investigating the microstructure of the copolymers CMA 5, 15, and 30 and CMM 5, 15, and 30.

Computer Simulation

The reactivity ratios of the AM-CMA and AM-CMM pairs determined by Gelabert,[5] Tanaka,[6] Yang,[7] and Baade[8] are listed in Table II.

The data from Gelabert[5] were introduced in the

Table II   Literature Values of the Reactivity Ratios $r1$ and $r2$ of the AM-CMA and AM-CMM Pairs

AM-CMA		AM-CMM		
$r1$	$r2$	$r1$	$r2$	Ref.
0.72	0.44	0.20	1.75	5
0.64	0.48	0.25	1.71	6
—	—	0.30	1.54	7
0.33	0.40	0.43	2.39	8

generalized copolymerization equation proposed by Ham.[9] We used the method proposed by Skeist[10] to follow the polymerization progress with conversion. The instantaneous composition of the copolymer is plotted against the initial monomeric composition, and the copolymerization progress is monitored by calculating the chemical composition and the sequence distribution of the monomeric structural units in the polymer backbone. In the case of the AM–CMA pair, the reactivity ratio values favored a statistically homogeneous copolymer exhibiting good alternation of the monomer units.

The instantaneous composition of the copolymer at the beginning of the copolymerization is not very different from the monomeric phase composition [Fig. 1(a)]. At the azeotropic point, the compositions are identical, i.e., [CMA] = 33.3%.

The instantaneous compositions remain virtually constant up to 90% conversion [Fig. 1(b)] in the case of CMA 15 and until the reaction is nearly completed (100%) in the case of CMA 30. The products obtained then have a homogeneous chemical composition.

Assuming that during copolymerization the addition of a monomer to the active macroradicals obeys Markov's first-order statistical model, the AM and CMA centered triad distributions were calculated as a function of the initial monomer feed composition.[4] The disparity between the triad fractions at the very beginning of the polymerization and when the degree of conversion approaches 100% reflects the drift in the chemical composition and in the monomeric sequence distribution during polymerization [Fig. 1(c)].
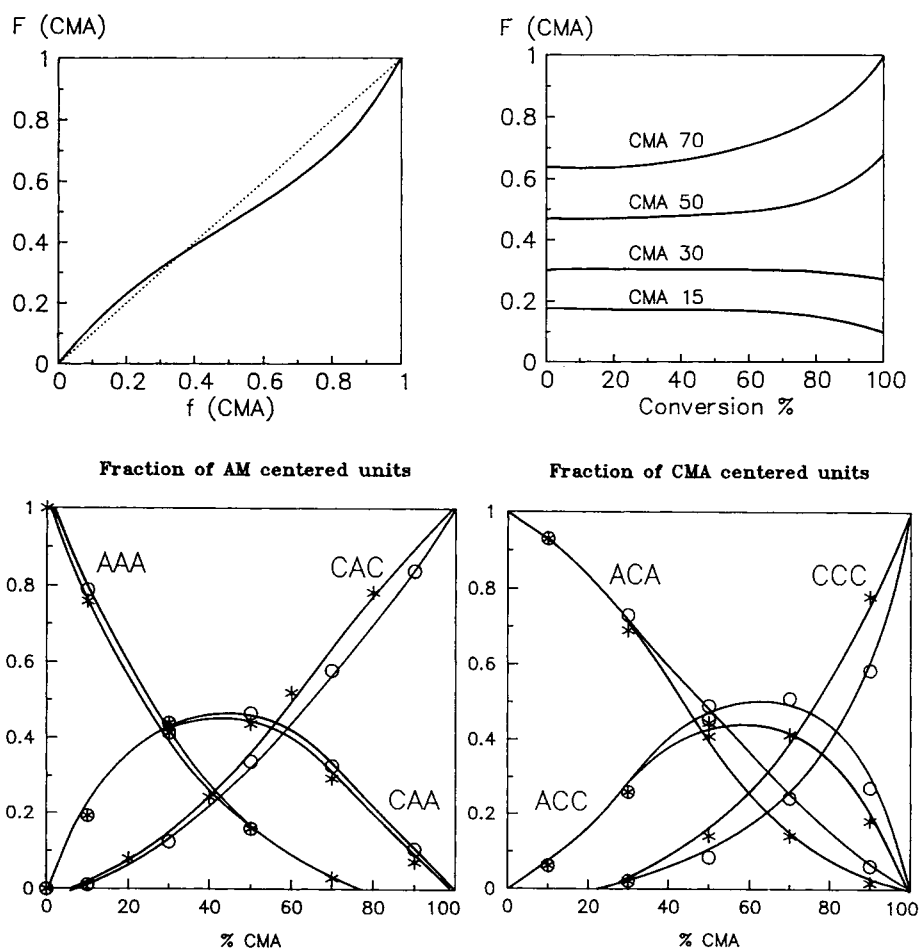

Figure 1   (a) Instantaneous composition (f_{CMA}, F_{CMA}) of the copolymer: CMA molar content in the monomeric and polymeric phases. (b) Instantaneous CMA content in the polymer as a function of conversion (%). (c) Fraction of AM and CMA centered triads in function of polymer composition: (— ○ —) 0%; (— * —) 100% conversion.

When examining the spatial distribution of neighbors of the AM units, we notice that the polymer is lightly richer in C–A–C (cationic–acrylamide–cationic) sequences at 100% conversion than at low conversion when the CMA content is beyond 35%. Below this value, the fractions are very close. The drift is more easily observed by examining the vicinity of the CMA units: The final polymer becomes richer in C–C–C sequences that form at the expense of A–C–C and A–C–A sequences, when the CMA content is beyond 35%.

The AM–CMM pair behaves differently: The values of the two reactivity ratios are quite different, and the polymerization should result in a heterogeneous polymer regardless the cationic monomer content. The macroradicals formed reacted preferably with the CMM monomer, and the copolymer obtained was richer in CMM than was the monomer feed composition [Fig. 2(a)].

The instantaneous compositions vary considerably as the reaction progresses: Being richer in CMM, the polymer initially formed uses up this monomer and, subsequently, AM homosequences are obtained. This drift is even more important as the initial CMM content is lower [Fig. 2(b)]. The drift in chemical composition of poly(AM–CMM) during polymerization is also illustrated in Figure 2(c).

For all cases investigated, the fractions of AM or CMM centered unit triads at the beginning and at the end of polymerization were quite different. All these data demonstrate the substantial heterogeneity of the AM–CMM copolymers, which was not the case for the AM–CMA copolymers.

Table III shows the calculated percentages of the AM, CMA, and CMM centered triads for the polymers CMA 5, 15, 30 and CMM 5, 15, 30 polymerized up to 100% conversion.

NMR Study of the Homopolymers

Poly(AM)

$$ -\!(C\beta H_2\!-\!C\alpha H)\overline{\,n\,} $$
$$ | $$
$$ CONH_2 $$
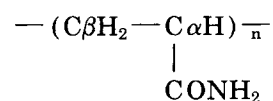
The tacticity of this homopolymer was characterized by several authors using ^{13}C-NMR.[11,12] In the case of a low molecular weight polymer, Lancaster and Connor[12] assigned the low-field and the high-field peaks, respectively, to rr and mm sequences of the $C\alpha$ carbon atom and the central peak to rm and mr sequences. The lines of the three unresolved patterns around the nucleus $C\beta$ are sensitive to configurational hexads. They also showed that the configurational propagation of meso m and racemic r dyads followed Bernouilli's statistics with $P(m) = 0.43$ and $P(r) = 0.57$.

Our results were obtained with a high molecular weight polymer ($M_w > 5 \cdot 10^6$). ^{13}C-NMR gives interesting information [Fig. 3(b)]. The carbonyl group exhibits a peak having a pattern of unresolved lines ($\delta = 180.2$–180.3 ppm), presumably corresponding to the syndiotactic rr and to the iso and heterotactic mm and mr triads. From the poor resolution of the lines, it can be suggested that the CO resonance remains virtually unaffected by tacticity. Furthermore, several lines can be observed forming three unresolved peaks at 42.6, 42.9, and 43.2 ppm around the $C\alpha$ carbon atom, which is sensitive to configurational triads and pentads, and also unresolved peaks at 35.2, 35.9, and 36.6 ppm around the $C\beta$ carbon atom, which is sensitive to hexads. Trace amounts of monomeric acrylamide can be detected from the presence of sharp lines at 129.2 and 130.6

Table III   Calculated Results (Simulation, Markov's First-Order Statistics) and Experimental Results (^{13}C-NMR) of the Percentage of Triads Centered around AM (A) and CMA or CMM (C)

% of Centered Triads	CMM 5		CMM 15		CMM 30		CMA 5		CMA 15		CMA 30	
	cal	^{13}C	cal	^{13}C	cal	^{13}C	cal	^{13}C	cal	^{13}C	cal	^{13}C
AAA	91	90	75	78.5	56	72	90	a	70	80	41.5	45
AAC + CAA	8.5	10	20	18.2	29	23	9.7	a	27	14.6	45.5	44
CAC	0.6	0	5.7	3.3	15	5	0.3	a	3	5.7	13	11
CCC	0	a	3	7	10	13	0	a	1	a	3	a
CCA + ACC	8	a	24	22	40	34	4	a	12	a	26	a
ACA	92	a	73	71	50	53	96	a	87	a	71	a

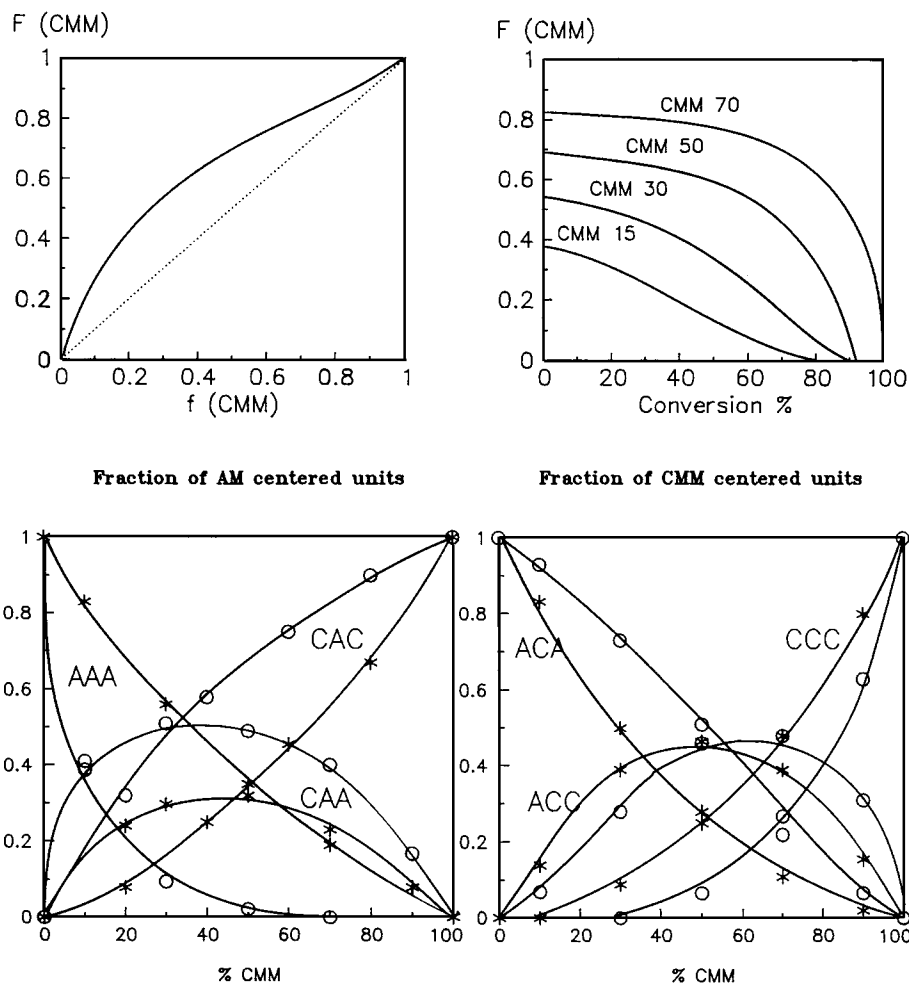a Quantification was not possible because of lack of spectral resolution.

Figure 2   (a) Instantaneous composition (f_{CMM}, F_{CMM}) of the copolymer: CMM molar content in the monomeric and polymeric phases. (b) Instantaneous CMM content in the polymer as a function of conversion (%). (c) Fraction of AM and CMM centered triads in function of polymer composition: (— O —) 0%; (— * —) 100% conversion.

ppm, corresponding to the $\underline{C}H$ and $\underline{C}H_2$ groups of acrylamide. The line at 178.2 ppm is characteristic of the carboxylic or imide groups and is indicative of a slight hydrolysis of the polymer. The specific chemical shifts of the C and H atoms of poly(AM) are summarized in Table IV.

Poly(CMA)

$$— (C\beta H_2 — C\alpha H) \frac{}{n}$$
$$|$$
$$COOCH_2CH_2N^{(+)}(CH_3)_3Cl^{(-)}$$
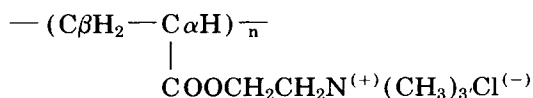
The ^{1}H-NMR spectrum is relatively simple, and in spite of a broadening of the resonance peaks resulting from the high molecular weight of the polymer,

each proton is readily distinguished [Fig. 3(a), Table V]. Furthermore, under the particular temperature and pH conditions that were used, an additional line appears at 3.15 ppm, which corresponds to $N(\underline{C}H_3)_3$ of choline chloride, freed by hydrolysis.

^{1}H-NMR spectroscopy is not as efficient as is ^{13}C-NMR for studying the polymer tacticity. ^{13}C-NMR shows that the $\underline{C}O$ group gives a sharp resonance line, and the $C\beta H_2$ group, a broad symmetrical resonance pattern, which reflects the low influence of tacticity. The $\underline{C}\alpha H$ carbon atom, sensitive to triads, gives three well-resolved peaks at 39.1, 40, and 40.8 ppm in the 26/48/26 ratio (Fig. 4). These lines are assigned to the mm, $mr + rm$, rr triads.

Statistical calculations carried out according to Pham[13] show that the propagation of dyads and triads occurs in accordance with Bernouilli's
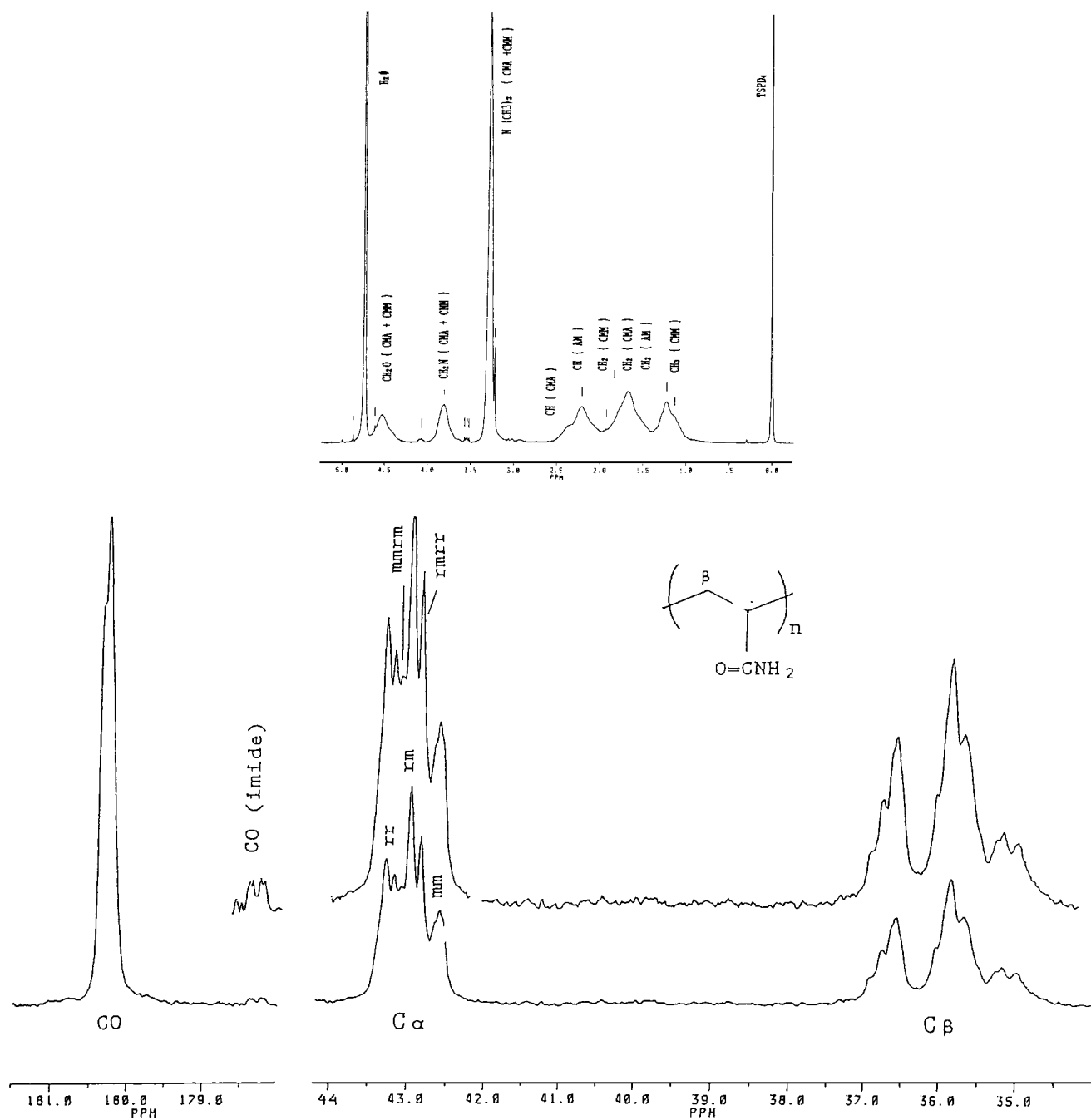
Figure 3   (a) ^{1}H-NMR spectrum of blends of homopolymers and copolymers AM–CMA–CMM. (b) ^{13}C-NMR spectrum of poly(AM).

model, with $P(m) = P(r) = 0.5$. The configuration of the propagating macroradical is then independent of the m or r nature of the end dyad. Furthermore, the probability of occurrence of m and r dyads is equal, and the configuration of the homopolymer is statistical. The chemical shifts of poly(CMA) are summarized in Table V.

Table IV ^{1}H- and ^{13}C-NMR Chemical Shift of Poly(AM)

	CH$_2$	CH	CO
^{1}H (ppm)	1.52	2.2	—
^{13}C (ppm)	35.6	42.9	180.2

Table V Poly(CMA): Spectral ^{1}H- and ^{13}C-NMR Assignments

	CβH$_2$	CαH	NCH$_2$	OCH$_2$	$^+$N(CH$_3$)$_3$	CO
^{1}H (ppm)	1.82	2.47	3.76	4.52	3.29	—
^{13}C (ppm)	33.2	40	64	57.4	52.4	173.6

Poly(CMM)

$$-(C\beta H_2-C\alpha(CH_3))\overline{}_n$$
$$\mid$$
$$COOCH_2CH_2N^{(+)}(CH_3)_3, Cl^{(-)}$$
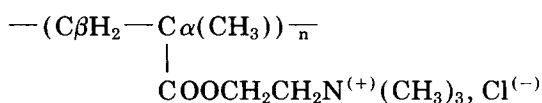
Poly(CMM) is readily identified by ^{1}H NMR, and the assignment of the resonance lines to protons of different functions offers no difficulty [Fig. 3(a)]. However, here again, the spectral resolution is not sufficient to characterize the tacticity of the polymer backbone. The ^{13}C-NMR spectrum on the contrary shows sharp lines around the $\underline{C}\alpha$, and α-$\underline{C}H_3$, and the $\underline{C}O$ carbon atoms, which are sensitive to triads and to pentads (Fig. 5). The well-resolved lines at

19.7, 20.4, and 22 ppm are assigned to rr, $(mr + rm)$, and mm sequences. By numerical integration of the different resonance lines, it can be verified that the configurational propagation of the dyads and triads obeys Bernouilli's model. An identification of the fine lines around the $\underline{C}\alpha$ and the $\underline{C}O$ carbon atoms is therefore possible by calculating the proportions of dyads, triads, or pentads[13] (Tables VI and VII).

The probability of occurrence of racemic and of meso dyads is on the average $P(r) = 0.76$ and $P(m) = 0.24$. Because of the steric hindrance due to the CH$_3$ group, the most likely propagation leads to r dyads. Table VIII summarizes the characteristic chemical shifts of the C and H atoms of poly(CMM).

Fig.4 ^{13}C NMR spectrum of poly(CMA)
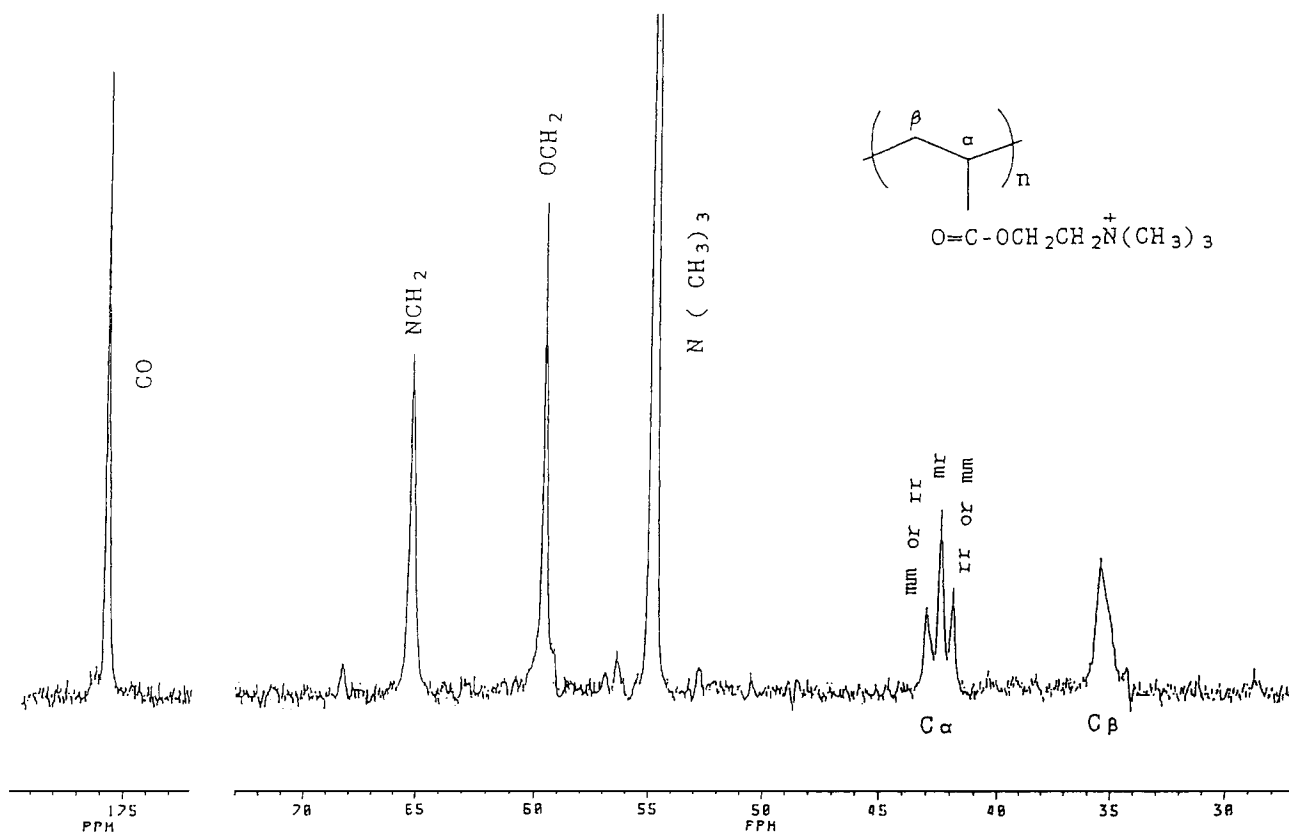
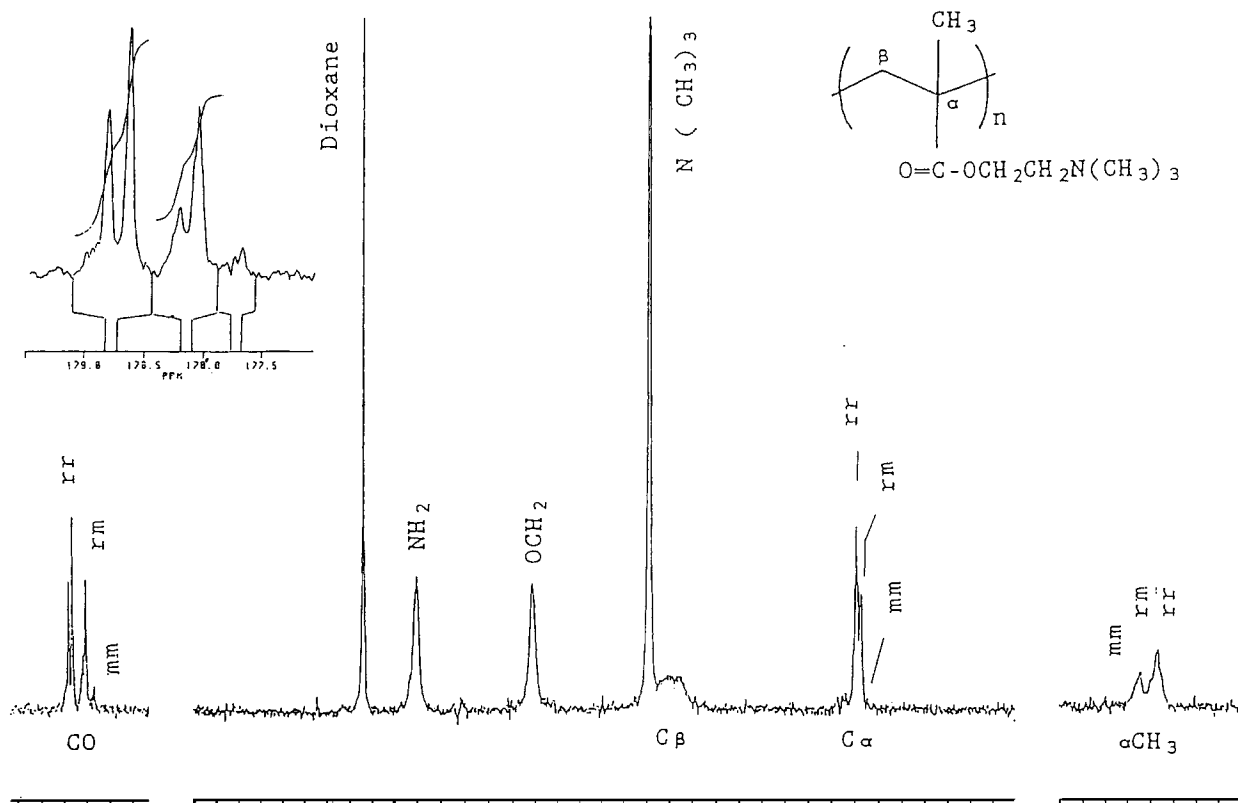**Figure 4** ^{13}C-NMR spectrum of poly(CMA).

Figure 5 ^{13}C-NMR spectrum of poly(CMM).

NMR Study of the Copolymers

The overall composition of the copolymers obtained by the inverse emulsion polymerization method was determined by elemental analysis (see Analytical Methods). The molar composition of the copolymer was calculated from chlorides and nitrogen determinations.

The chemical composition can also be monitored with ^{1}H-NMR in a D$_2$O solution, by integrating the N(C$\underline{\text{H}}_3$)$_3$, the C$\underline{\text{H}}_2$, and the C$\underline{\text{H}}$ signals. These measurements are valid in the case of poly(AM–CMA) and poly(AM–CMM) copolymers.

A prerequisite for the quantitative determination of the copolymer composition and microstructure by ^{13}C NMR is that the perturbations due, on the one hand, to the NOE effect be eliminated through the use of pulse sequences with gated decoupling and, on the other hand, those due to the longitudinal relaxation time $T1$ be eliminated by adding relaxation agents, such as Cr^{3+} or Fe^{3+} complexes.[14] It is known that the data collected through ^{13}C NMR analysis are quantitative provided the same type of carbon atom (i.e., Cβ, Cα, CO, or CN) is taken into consideration.[13] Finally, the Overhauser effect between Cα and Cβ atoms becomes negligible in the

case of aqueous solutions of high molecular weight polymers.

We checked that under our conditions, all the carbon atoms investigated gave a quantitative response. It is possible to determine quantitatively by ^{13}C-NMR each monomeric component either on the basis of the ester/amide $\underline{\text{C}}$O sequences for both types of polymers (Figs. 6 and 7) or on the basis of the ester O$\underline{\text{C}}$H$_2$ and of the (ester + amide) $\underline{\text{C}}\beta$H$_2$ for poly(AM—CMA), and on the basis of the ester O$\underline{\text{C}}$H$_2$ and of the amide $\underline{\text{C}}\beta$H$_2$ sequences for poly(AM–CMM) [Figs. 3(b), 4, and 5].

The analytical results are summarized in Table IX. The chemical compositions obtained by elemental analysis are very close to those obtained by NMR, in particular, by ^{13}C NMR. This is due to the sharpness of the peaks, which facilities their numerical integration.

Validation of the Copolymers' Sequence Distribution and Discussion

Poly(AM–CMA) Copolymer

We focused our attention on the analysis of the microstructure around the $\underline{\text{C}}$O groups of the ester and

Table VI   Poly(CMM)—Identification of Triads around the $\underline{C}$ α Carbon Atom by ^{13}C-NMR

Triads	rr	$(mr + rm)$	mm
^{13}C (ppm)	45.98	45.74	45.3
Calculated	0.56	0.39	0.05
Found (^{13}C)	0.60	0.35	0.03

amide functions. The only publication on this subject is that of Lafuma and Durand[15] dealing with the cationic copolymers AM–CMA. The spectra corresponding to AM and CMA 5, 15, and 30 polymers are illustrated in Figure 6. In these copolymers, a peak with unresolved lines appears at the $\underline{C}$O groups of the amide (δ = 180 ppm) and of the ester functions (δ = 173.6 ppm). The peak corresponding to the ester $\underline{C}$O is virtually symmetrical when the polymer contains 30% of the cationic units (CMA 30).

The carbonyl resonance pattern that was observed is sensitive to compositional heterogeneity effects. One can calculate the respective proportions of the triads centered around the investigated nucleus (Table III). Therefore, it is possible to assign the following chemical shifts to the triads centered around the amide $\underline{C}$O:

$$
\begin{array}{ll}
\text{A}\underline{\text{A}}\text{A} & \delta = 180.2 \text{ ppm} \\
(\text{A}\underline{\text{A}}\text{C} + \text{CAA}) & \delta = 179.9 \text{ ppm} \\
\text{C}\underline{\text{A}}\text{C} & \delta = 179.7 \text{ ppm}
\end{array}
$$

It can be seen that the vicinity of a cationic monomeric unit leads to a high-field shift of the amide $\underline{C}$O signal, whereas the opposite effect is observed when the comonomer of AM is sodium acrylate.[16,17] No assignments of the ester $\underline{C}$O centered triads were attempted due to poor spectral resolution.

The relative proportions of each peak corresponding to the triads have been estimated by peak deconvolution of the spectral curves using the Bruker Linesim computer program. The pattern relative to the amide $\underline{C}$O group is assumed to be the sum of three peaks with Lorentzian profiles. Although the choice of the peaks' profiles remains arbitrary, the result of the simulation is in agreement with the NMR analysis (Table III). In our opinion, the copolymerization of AM and CMA follows Markov's first-order statistics.

Poly (AM–CMM) Copolymer

The spectra corresponding to CMM, CMM5, CMM 15, and CMM 30 polymers are illustrated in Figure 7. A multiplet resonance pattern appears at the amide CO and is composed of three broad unresolved peaks on the low-field side of the poly(AM) carbonyl group. Related to the compositional heterogeneity of the copolymers, this effect is enhanced by the presence of the $\alpha\underline{C}$H$_3$ group of CMM. Cationicity causes a progressive broadening of the resonance peaks as the CMM content increases. Once the peaks are separated by deconvolution and are integrated, we notice a small discrepancy between the experimental and calculated values found for the

Table VII   Poly(CMM)—Identification of the Triads and Pentads around the $\underline{C}$O Carbon Atom by ^{13}C-NMR

Pentads	$mrrm$	$mrrr$	$rrrr$	$mrmm$	$mrmr$ + $rrmm$	$rrmr$	$mmmm$	$rmmm$	$rmmm$
^{13}C (ppm)	178.9	178.8	178.6	178.3	178.2	178	177.8	177.7	177.6
Calculated	0.03	0.21	0.32	0.02	0.13	0.21	0.01	0.02	0.03
Found (^{13}C)	0.05	0.2	0.3	0.02	0.11	0.25	0.01	0.02	0.03
Triads		$rr = 0.55$			$rm = 0.38$			$mm = 0.05$	

Table VIII ^{1}H- and ^{13}C-NMR Chemical Shifts of Poly(CMM)

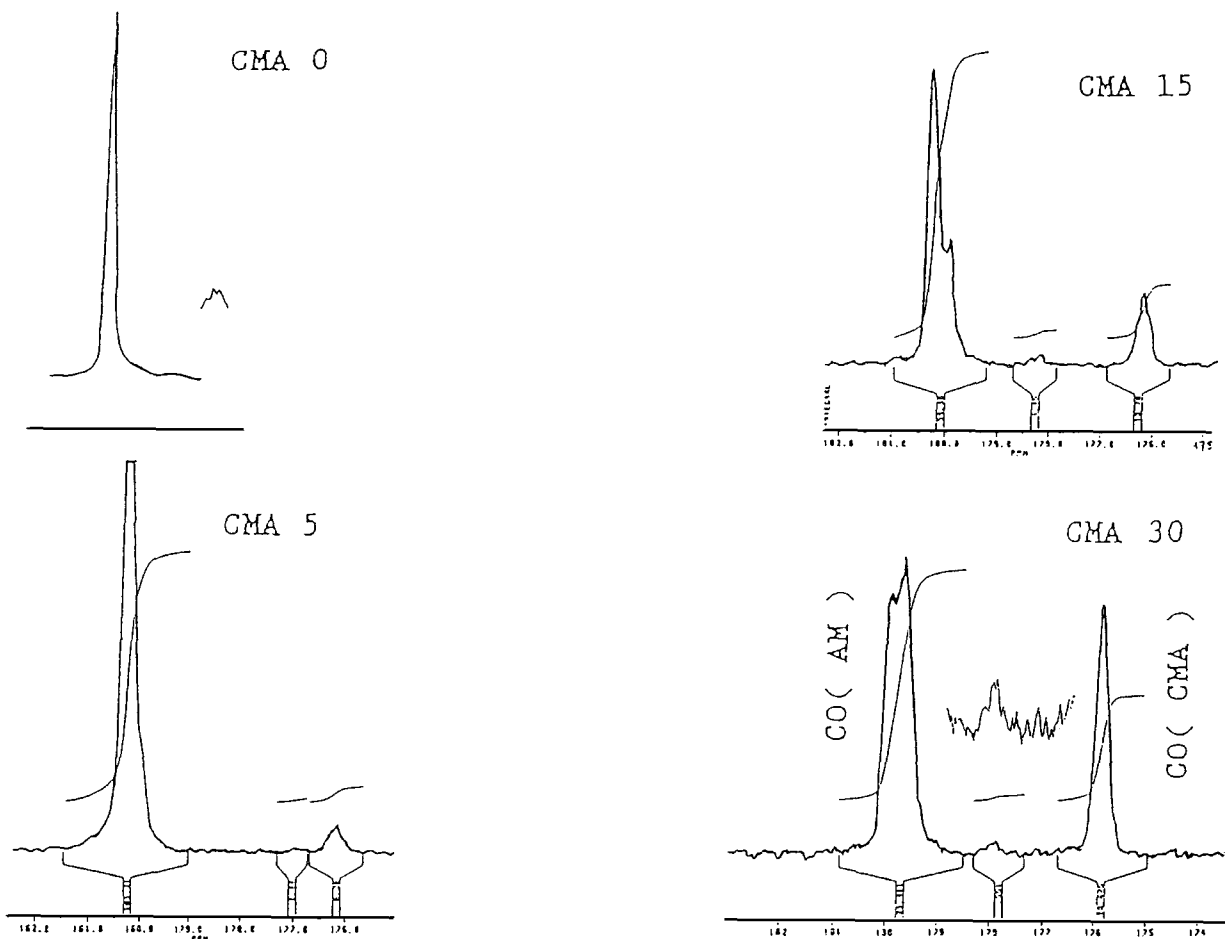|	CH$_3$	CβH$_2$	C	OCH$_2$	NCH$_2$	$^+$N(CH$_3$)$_3$	CO
^{1}H (ppm)	1.25	2.1	—	4.53	3.85	3.25	—
^{13}C (ppm)	19.7	54	45.9	60.1	65	54.9	178

Figure 6   ¹³C-NMR resonance patterns of the CO groups in copolymers containing 0, 5, 15, and 30% CMA.

amide C̲O centered triads, confirming then the validity of Markov's model (Table III) when AAM is copolymerized with CMM.

In table X we have summarized the values of the chemical shifts corresponding to the chemical triads AA̲A, (CA̲A + AA̲C) and CA̲C. The assignment of the resonance multiplets related to the ester CO is more difficult, because to the tacticity of long CMM homosequences is added the cotacticity of the poly(AM-CMM) copolymer. However, the examination of copolymers with a variable CMM content shows that the resonance signals corresponding to the ester C̲O move in the direction of higher fields when the CMM content decreases.

In the case of CMM 5, the cationic monomer units are isolated between AAM units, and, therefore, the AC̲A triads formation is favored. The multiplets observed at 177.45, and 177.2, and apparently at 176.7 ppm, are related to the cotacticity effect. Quite sim-

ilar to the homopolymer tacticity, they are assigned as the syndio (AC̲A) or r'r', hetero (AC̲A) or m'r'/r'm', and iso (AC̲A) or m'm' sequences.

In the case of CMM 15, three groups of multiplets are found at 179, 178.2, and 177.45 ppm. The simulation gives the relative proportions of the CC̲C triads: 3% (AC̲C + CC̲A):24%, AC̲A:73%. These values are close to the experimental results (7/22/71).

In the case of CMM 30, a pattern of unresolved peaks is observed with three peaks at 179, 178.2, and 177.45 ppm. The simulation of the triads CC̲C/AC̲C + CC̲A/AC̲C gives 10, 40, and 50%. These values are close to the experimental results obtained on the deconvoluted peaks: 13, 34, and 53%.

We have summarized in Table X the chemical shifts of the CO resonance lines corresponding to the different AM and CMM centered triads. We did not attempt to characterize the unresolved lines at
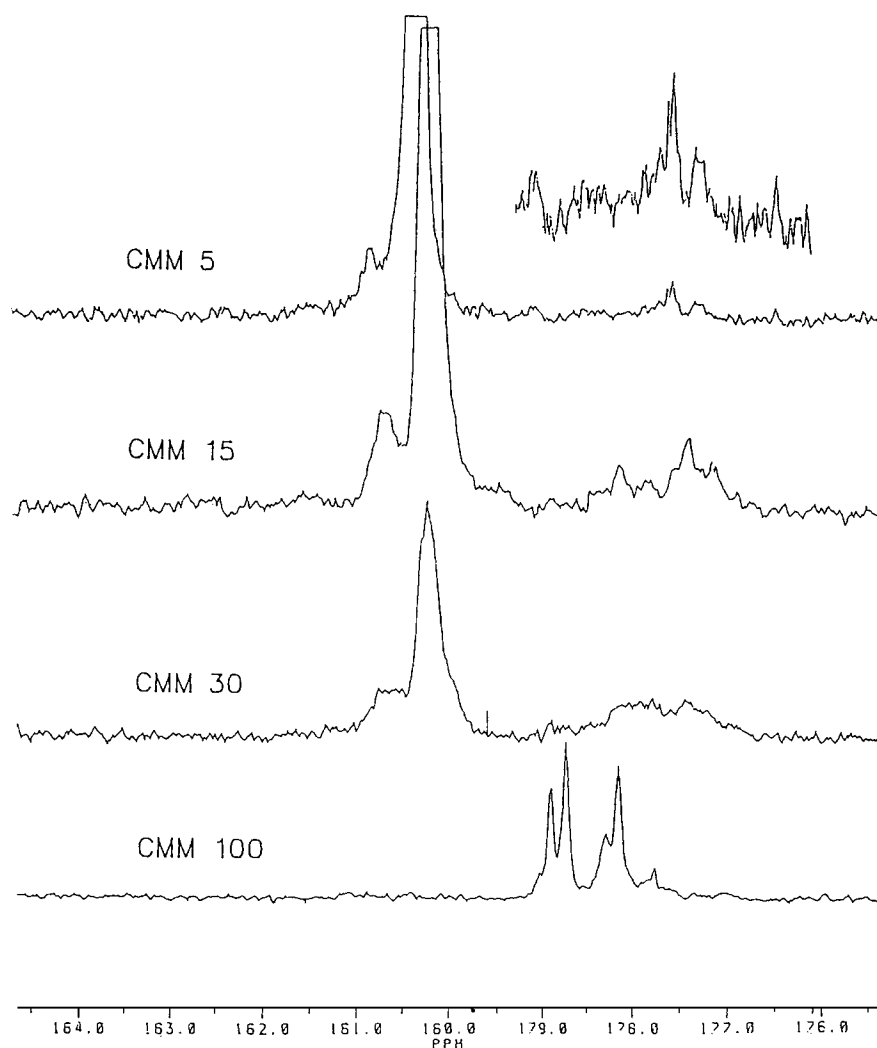
Figure 7   ¹³C-NMR resonance patterns of the CO groups in copolymers containing 5, 15, 30, and 100% CMM.

the $\underline{C}H_2$ and $\underline{C}H$ carbon atoms of AM that are shifted by the presence of the CMM units. Furthermore, other additional signals are observed when the temperature is raised or the pH is changed. They correspond to the formation of a cyclic imide between AM and CMA units[15] or simply to the

Table IX   Comparative Chemical Compositions Resulting from Different Analytical Methods

	% CMA or CMM			
	CMM 15	CMM 30	CMA 15	CMA 30
Theoretical	15	30	15	30
Cl⁻/N	16.2	32	15.2	31.2
By ¹H-NMR	18.5	33	20	31.7
By ¹³C-NMR ($\underline{C}$O)	15.5	31.5	13	27
By ¹³C-NMR ($O\underline{C}H_2$, $\underline{C}\beta H_2$)	15.6	32.9	—	—

Table X   Identification of the Lines around the Carbonyl Groups (C̲O) of the AM–CMM Copolymers

CO (AM)		CO (CMM)	
Triad	δ ppm	Triad	δ ppm
AA̲A	180.2	CC̲C	
		r'r'	178.8
CA̲A (AA̲C)	180.75	*m'r'*	178.2
		m'm'	177.7
CA̲C	181.4	CC̲A (AC̲C)	
		r'r'	178.2
		m'r'	177.5
		m'm'	177
		AC̲A	
		r'r'	177.45
		m'r'	177.2
		m'm'	176.7

hydrolysis of the cationic monomer.[18] We will examine in a future study the possibility of monitoring the degradation of these polymers by NMR spectroscopy.

CONCLUSIONS

In this work, we have shown that ^{13}C-NMR is a powerful tool for analyzing the tacticity of acrylic homopolymers and the cotacticity of acrylamide/acrylate copolymers. The configurational propagation of the dyads and triads follows Bernouilli's statistical model in the case of homopolymers: $P(m) = 0.43$, $P(r) = 0.57$ for poly(AM); $P(m) = P(r) = 0.50$ for poly(CMA) and $P(m) = 0.24$, $P(r) = 0.76$ for poly(CMM). In the case of copolymers obtained by the inverse emulsion polymerization technique from acrylamide and cationic acrylic monomer (CMA or CMM), the distribution of the monomeric sequences obeys to Markov's first-order statistics.

There is good agreement between the calculated chemical sequences distribution and that obtained experimentally by ^{13}C-NMR. Computer simulations are particularly useful for obtaining these results as well as for simulating the copolymerization of AM/cationic monomer. The chemical composition obtained from spectral analysis was found to be in good agreement with another analytical method such as elemental analysis. In addition, it clearly appears

that the chemical microstructure of the AM/CMA copolymers indicates a homogeneous distribution of the monomer units along the polymer backbone, which is not the case of the copolymers AM/CMM that exhibit a far more heterogeneous microstructure.

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