identified tetrad is needed among the four. Tests show

$$\alpha\delta^+(\mathrm{EBEE}) = k[\mathrm{EBEE}] \quad (58)$$

to be the most suitable choice. Finally, we have eq 56 and 57 to combine with yet another needed independent identification to form the third group. In this case $\alpha\alpha$(EBBE) proves to be the best choice in region A:

$$\alpha\alpha(\mathrm{EBBE}) = k[\mathrm{EBBE}] \quad (59)$$

With only the three additional measurements discussed above, the triad analysis can be extended to a complete set of tetrads. Other direct tetrad measurements are possible as the $\alpha\alpha$ carbons, the $\alpha\gamma$ and $\alpha\delta^+$ carbons, and the $\gamma\gamma$ and $\gamma\delta^+$ carbons are clearly associated with tetrad sequences. It is better, however, to restrict the tetrad measurements to distinct, well-defined resonances as errors introduced from any single meassurement are carried over into the determination of the rest.

The quantitative methods presented in this study were designed to minimize errors arising from line broadening, uncertainties in configurational assignments, peak overlap, phasing, and differences in line widths. The utilization of broad spectral regions with complete, collective assignments and appropriate well-defined single resonances have eliminated many of these problems and has led to quantitative results which are internally consistent. When larger diameter probes are used, there may be a loss of spectral resolution. In such cases, it is likely that regions C and D will not be well separated. As a result, one should not utilize either methods A or B but combine regions C and D into one collective area. Equations 3c, 8, 9d, and 19, along with those describing regions C and D, can be used to determine more accurately a triad distribution.

A triad analysis is all that is needed to determine relative comonomer concentrations, average sequence lengths, and run numbers; all can be accurately obtained for the ethylene-1-butene copolymers. A tetrad distribution is available from the carbon-13 NMR data but will generally not be so accurate as the triad distribution as a further delineation of closely spaced resonances is required. With this reliable quantitative information, the polymer chemist is in a position to correlate various structural moieties with the observed density, flexural modulus, and other physical properties.

Acknowledgment. We express our appreciation to Mr. J. R. Donaldson for the experimental carbon-13 NMR measurements.

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Synthetic Polyampholytes. 2. Sequence Distribution in Methacrylic Acid-(Dimethylamino)ethyl Methacrylate Copolymers by ^{13}C NMR Spectroscopy[†]

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ABSTRACT: The ^{13}C NMR spectra of methacrylic acid-(dimethylamino)ethyl methacrylate copolymers in NaOD solution show a triad structure which is due solely to a copolymeric distribution without any tacticity effect for the carbonyl pattern (ionized acid or ester group). This permits assignments and sequence measurements. Polyampholytes prepared by radical-initiated copolymerization have a slight alternating tendency. Polyampholytes obtained by hydrolysis of poly[(dimethylamino)ethyl methacrylate] in concentrated sulfuric acid have a blocklike distribution of acid sequences which passes through a maximum as their acid content F_A is increased. Alkaline-hydrolyzed polyampholytes (2-propanol/KOH/H_2O in excess) also show a slight tendency to have a blocklike structure, which is greater in the beginning of the hydrolysis and tends toward randomness as the reaction progresses. Solubilities and apparent p*K*s of the polyelectrolytes are discussed in terms of their microstructures.

Introduction

^{13}C NMR spectroscopy is an effective technique for measuring, or at least estimating, the triad composition in a copolymer: the differential nuclear Overhauser effect (NOE) enhancement is approximately equal for similar carbons within different types of chemical sequences.[1] It is also generally admitted that for nonprotonated carbons with restricted mobilities like in polymers, the residual spin-lattice relaxation times (T_1) are of the same order.[1] These assumptions, even if not exactly true as shown by Klesper et al.[2] for the methacrylic acid-methyl methacrylate copolymers (no difference detected in the NOE of COOH and $COOCH_3$ but differences in T_1), are the basis of studies of copolymer structures by ^{13}C NMR spectroscopy.

Very few NMR studies have been devoted to synthetic polyelectrolytes in aqueous solution. This is due to the insufficient definition of resonance signals that is generally obtained due to the large number of compositional-con-

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Table I
Insolubility Range of
Methacrylic Acid-(Dimethylamino)ethyl Methacrylate Copolymers Prepared by Different Methods

% A	without NaCl (in pure water)	with 1 N NaCl
	1. Copolymers Prepared by Acid Hydrolysis of Poly[(dimethylamino)ethyl methacrylate]	
5	s[a]	i,[a] pH >9.5
9	s	i, pH >9.5
27	s	s
42	s	s
50	i, 4.5 < pH < 7.2	s
68	i, 4 < pH < 5.2	i, 3 < pH < 4.2
81	i, 3.5 < pH < 4.5	i, 2.8 < pH < 5
94	i, 2.7 < pH < 3.2	i, 2.3 < pH < 4.6
95	i, 2.7 < pH < 3.4	i, 2.7 < pH < 4.8
100	entirely soluble	
	2. Copolymers Prepared by Alkaline Hydrolysis of PDMAEM	
7	i, pH >9	s
20	s	s
37	8, 7.7 < pH < 8.4	slightly turbid, 8.0 < pH < 8.2
56	i, 4.6 < pH < 6.1	i, 3.2 < pH < 5.5
61	i, 6 < pH < 4.4	i, 4.8 < pH < 5.6
75	i, 4.3 < pH < 6.1	i, 3.9 < pH < 5.6
	3. Copolymers Prepared by Radical-Initiated Copolymerization of MA and DMAEM	
	entirely soluble all over the pH range for % A > 20	

[a] s = soluble; i = insoluble.

figurational sequence possibilities. Schaefer[3] described ^{13}C NMR spectra of poly(methacrylic acid) (PMA), poly(acrylic acid), and an alternating poly(ethylene–maleic anhydride) copolymer. He obtained a significant titration of these polyelectrolytes by plotting the chemical shift or the peak width of the carboxyl carbon resonance in terms of pH as in an ordinary potentiometric titration. Resonances due to tacticity effects were evident in the spectra when the polymers were dissolved in acidic solutions.

No ^{1}H NMR or ^{13}C NMR studies have been done on synthetic polyampholytes. The ^{23}Na relaxation rate and chemical shift have been measured as a function of pH for a random methacrylic acid–(dimethylamino)ethyl methacrylate copolymer.[4] A marked increase of these parameters was noted for a degree of ionization $\alpha = 0.2$ in relation to cooperative conformational transition of methacrylic acid units.[4]

We have reported recently the preparation and potentiometric properties of polyampholytes obtained by free radical copolymerization of methacrylic acid (MA) and (dimethylamino)ethyl methacrylate (DMAEM) or by hydrolysis of poly[(dimethylamino)ethyl methacrylate] (PDMAEM) with a 2-propanol/KOH/water mixture or with concentrated sulfuric acid.[5,6] These polymers differ in their neutralization curves, their apparent p*K*s, and their solubilities in terms of pH. The purpose of this paper is to show that this behavior is related to the distribution of different compositional triads in polymers prepared in different ways. A comparison of the alkaline or acid hydrolysis mechanism of PDMAEM with that of poly(methyl methacrylate) (PMMA) hydrolysis is possible from these results.

Experimental Section

The preparation and potentiometric data of the polyampholytes studied in this work have been described elsewhere.[5] The copolymers C_1 and C_3 have been prepared by free radical polymerization. The series A_1–A_7 designates the polyampholytes obtained by acidolysis. The series B_1–B_5 refers to those obtained by alkaline hydrolysis. In all cases, the monomeric acid units are designated by A, and the monomeric basic units by B. Their solubility behavior is described in Table I.

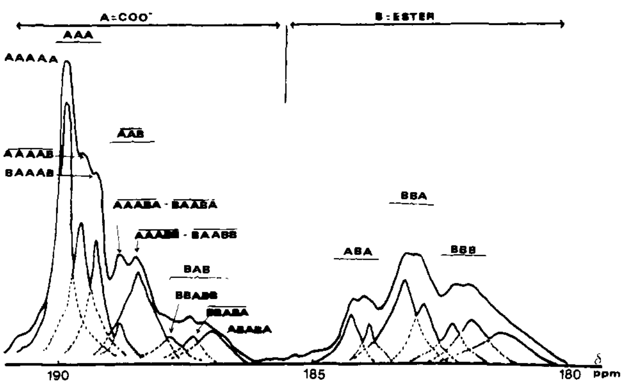

Figure 1. Example of resolution and interpretation of an expanded ^{13}C NMR spectrum: sample A4 (% A = 69). Details of deconvolution.

For the NMR measurements, copolymers (250 mg) were dissolved in D_2O, and 2 N NaOD was added in slight excess to neutralize the acid function and to obtain a solution of 20 wt % polymer. The dissolution could take 24 h. The spectra of the resulting viscous opaque solutions, flushed with N_2, were recorded with a WH90C Bruker spectrometer at 22.63 MHz, locked on D_2O with a frequency range of 6000 Hz on 8K; the number of transients was above 60 000 for the copolymers in the expanded carboxyl region (×20). All chemical shifts are expressed in ppm downfield from external Me_4Si.

Curves were resolved into their components with a DuPont 310 curve resolver. This instrument approximates each peak to a Lorentzian shape. Care must be taken in the interpretation of such results since there may not be a unique solution if one or more peaks are poorly resolved in spectra. The surface of each triad is the sum of each substructure (Figure 1).

Results and Discussion

Radical-Initiated Copolymerization. On the basis of the terminal-unit copolymerization model following the well-known equation of Alfrey and Mayo, the entire sequence distribution of a copolymer can be predicted for low conversion.

The instantaneous copolymer composition $F_A/F_B = y$ is related to the monomer feed $f_A/f_B = x$ by the equation

$$y = x[r_A f_A + f_B]/[r_A f_B + f_A]$$

where r_A and r_B are the reactivity ratios. These parameters have been calculated for MA–DMAEM polyampholytes, using the accurate Kelen–Tüdös linearization method.[7]

The data indicate that the experimental values between 0 and 80% of amine monomer fit well the theoretical curves of copolymer composition vs. monomer feed using $r_A = 0.45$ and $r_B = 0.98$. The results are confirmed by applying Chûjô's method,[8] in which the reactivity ratios can be determined from a single sample of a copolymer AB if the molar fractions of each dyad (F_{AA}, F_{AB}, F_{BB}) are known; e.g., from ^{13}C NMR data of sample C_1 (Table III), we found $r_A = 0.42$ and $r_B = 1.02$, illustrating that the assignments made in the interpretation of the NMR spectra are justified.

The terminal model is suitable for the MA–DMAEM/methanol/water system, at least up to an 80% amine feed (corresponding to pH 8.52) and not just for the cases where the monomeric ratio acid/amine ≤1 as was mentioned earlier by Ehrlich.[9] For the very rich amine monomeric mixture (≥80%), the system contains three components (DMAEM in excess and MA–DMAEM salt that is mainly dissociated into ionized MA and protonated amine). The rate of DMAEM polymerization seems unaffected by pH

Table II
Reactivity Ratios of MA-DMAEM Copolymers

copolymer	r_A	r_B	r_B/r_A	conditions	ref
MA-DEAEM[a]	0.52	1.28	2.46	methanol/water, $K_2S_2O_8$	10a
MA-DEAEM[b]	0.98	0.90	0.92	pH 1.2, $K_2S_2O_8$	10a
MA-DEAEM[b]	0.08	0.65	8.12	pH 7.2, $K_2S_2O_8$	10a
MA-DMAEM	0.45	0.98	2.18	methanol/water	this work
MA-DMAEM	0.67	3.0	4.48	methanol (AIBN)[c]	9

[a] Calculated by Kelen-Tüdös extrapolation with data of Alfrey.[10] [b] Calculated by Alfrey et al.[10] [c] In the presence of *n*-butyl mercaptan.[9]

according to Alfrey et al.,[10a] unlike the polymerization of MA, which decreases with increasing ionization, the rate approaching zero at pH 7 (Table II). But the copolymerization becomes much slower with a large excess of tertiary amine. Moreover, the resolution of the ^{13}C NMR spectra of the amine-rich copolymers drops, presenting no interest for this study.

The Kelen–Tüdös linear method is also used to calculate the reactivity ratios of (diethylamino)ethyl methacrylate (DEAEM–MA) copolymers, from data of Alfrey et al.,[10a] and gives $r_A = 0.52$ and $r_B = 1.28$ (Table II). DMAEM copolymerizes a little more slowly with MA than DEAEM ($r_B/r_A = 2.18$ for MA–DMAEM and $r_B/r_A = 2.46$ for MA–DEAEM).

Spectral Assignments of Methacrylic Acid–(Dimethylamino)ethyl Methacrylate Copolymers. Homopolymers (PMA and PDMAEM). Carbonyl carbon resonance spectral assignments are made by comparison with those of PMA and PDMAEM, both in 2 N NaOD solution. According to Schaefer,[3] in basic medium the PMA spectrum is very well resolved and simple to interpret.[3] *No tacticity effect can be observed in the narrow carbonyl peak* at 189.1 ppm downfield from Me_4Si (Figure 2-1a). The carbonyl carbon resonance yields triad information when the spectra of PMA in acid solution are observed. The results obtained (% $r = 62$) are in agreement with results found employing the quaternary carbon resonance pattern as shown by Schaefer,[3] or from the carbonyl or α-CH_3 patterns in pyridine-d_5 solution.[11]

For PDMAEM in NaOD solution, the resolution remains mediocre even with numerous scans. Peak assignments are made with the aid of off-resonance decoupling on the polyamine hydrochloride for which the resolution is much better. The $(CH_3)_2N$ carbon shift is not very sensitive to pH ($\Delta\delta = 1.3$ for the chemical shift differences in acidic and basic media). The carbonyl ester peak, located at 179.1 ppm in the spectrum of the polyamine in 2 N NaOH solution, shows *no fine structure due to the tacticity*, whereas a triad assignment can be made from the spectrum of the polyamine in DCl solution (Figure 2-2b) (rr, mr, and mm at 179.4, 178.2, and 177.4 ppm, respectively; relative proportion = 56.2/35.9/7.9%). This assignment is made by comparison with that of PMA because tactic PDMAEMs are not known. Following the carbonyl pattern, which is also not very sensitive to pH ($\Delta\delta = 1.1$), the radical-initiated PDMAEM seems more syndiotactic (% $r = 74$) than PMA. The attribution of one methylene near the oxygen (OCH_2) and the other near the amine (CH_2N) remains ambiguous because the methylene strongly overlaps either one or the other.[5]

Polyampholytes (MA–DMAEM Copolymers). From these observations, we believe that any fine structure noted in the carbonyl carbon resonance patterns of the copolymers, in NaOD solution will not be due to a *tacticity effect but merely to a copolymeric effect.* This enables the carbonyl carbon spectra of (MA–DMAEM) copolymers to be interpreted in terms of triads.

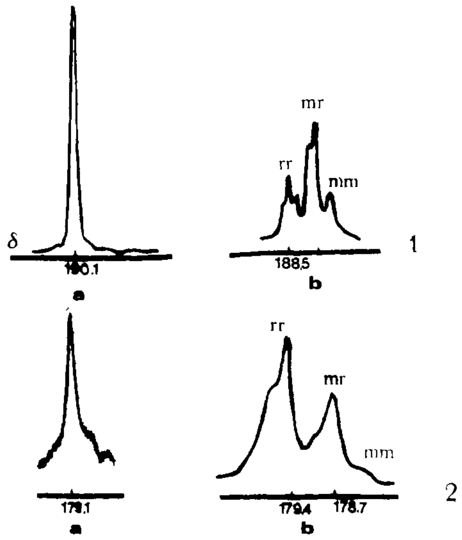

Figure 2. Expanded ^{13}C NMR spectra of homopolymer carbonyls: (1) acid group of PMA; (2) ester group of PDMAEM. (a) In NaOD; (b) in DCl.

The interpretation was also made by comparison with the more detailed results of Klesper et al.[11] on methyl methacrylate–methacrylic acid (MMA–MA) copolymers, in which both tacticity and copolymeric effects occur, as is often the case for copolymers. These authors determined all six possible triads of monomeric units as individual peaks in the methyl region first by ^1H NMR[2] and then by ^{13}C NMR studies of the polymer in pyridine-d_5 solution.[11] Assignments of atactic copolymers were made by comparison with known chemical shifts of pentad–triad sequences in pure syndiotactic or isotactic MMA–MA copolymers. Copolymers obtained by half-esterification of atactic poly(methacrylic anhydride) with methanol showed a tendency toward alternation and those prepared by hydrolysis of atactic PMMA with pyridine–H_2O at high temperature yielded moderately blocklike atactic copolymers.

Figure 3 presents the expanded carbonyl region of the ^{13}C NMR spectra of MA–DMAEM copolymers between 180 and 190 ppm in 2 N NaOD solution: Figure 3A shows the spectra of the A_1 to A_7 series of copolymers obtained by acidolysis, with acid contents of 28, 42, 60, 69, 78, 89, and 95 mol %, Figure 3B shows the spectra of the B_1 to B_5 series of copolymers obtained by alkaline-hydrolysis, with acid contents of 37, 48, 56, 66, and 75 mol %, and Figure 3C shows the spectra of two radical-initiated copolymers (C_1 and C_3, as examples), with acid contents of 40 and 60 mol %.

For amine-rich copolymers (for about %A $\simeq$ 25), the spectral resolution remains too poor to make any assignments. Simple inspection of this series of spectra has enabled two main peak structures to be assigned as follows: the lowest field peak is due to the ionized carbonyl of the acid unit A and the highest is due to the ester carbonyl

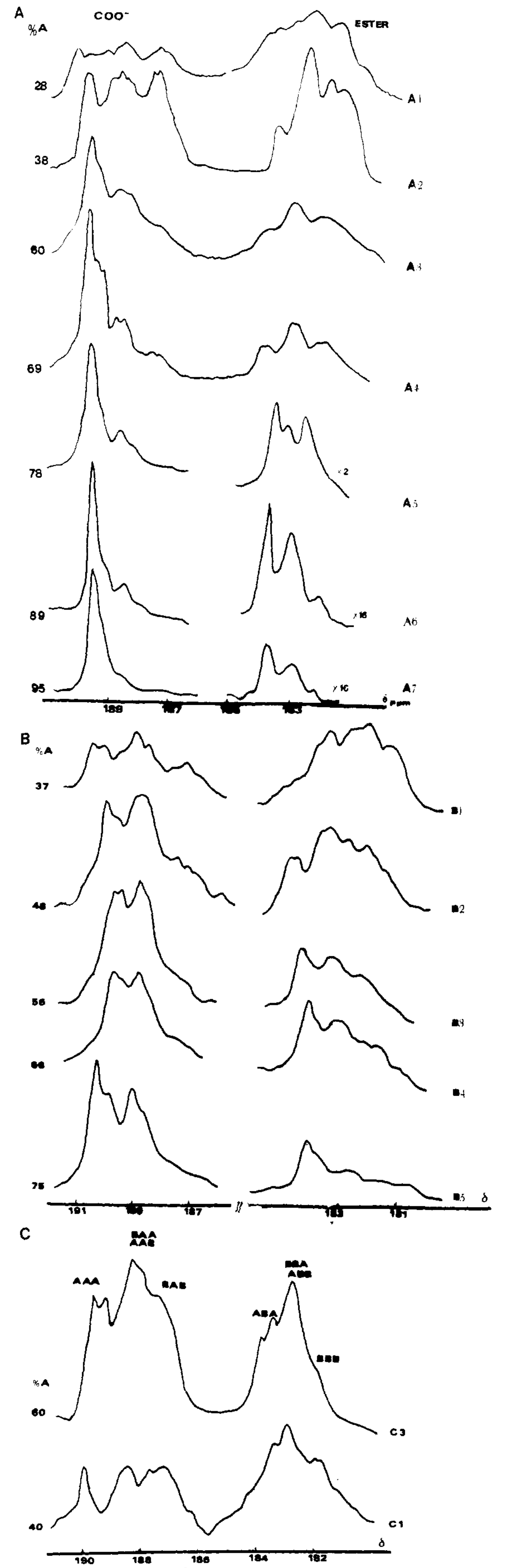

Figure 3. Expanded ^{13}C NMR spectra of polyampholyte carbonyls (in 2 N NaOD): (A) obtained by acidolysis (traces 1–7: % A = 28, 42, 60, 78, 89, and 95, respectively); (B) obtained by alkaline hydrolysis (traces 1–5: % A = 37, 48, 56, 66, and 75, respectively); (C) obtained by radical-initiated copolymerization (traces 1 and 3: % A = 40 and 60, respectively).

of the basic unit B by comparison with homopolymers. In all expanded spectra, different triad sequences are clearly visible and for some of them, especially trace A_4, a pentad assignment could be made (Figure 1).

From low to high field, we have respectively the A-centered triads AAA, $\overline{\text{AAB}}$, and BAB for the A peak and the B-centered triads ABA, $\overline{\text{BBA}}$, and BBB for the B peak. The bar refers to the sum of two triads, the forward and the reverse triads, which are not distinguishable by NMR (e.g., AAB = BAA); the same is true for AB dyads. As the acid content increases, the A and B peaks draw nearer to each other by about 2 ppm. A good separation of the A- and B-centered triads makes the determination of F_A easier, in good agreement with the determination obtained by IR spectra of polyampholyte salts or by potentiometry[4] and justifies the assumptions made about the relaxation time as mentioned in the Introduction:

$$\% F_A = 100 \times A_A/|A_A + A_B|$$

where A_A and A_B are the areas of the COO⁻ and the carbonyl ester peaks.

Sequence Distribution Measurements (Relation with Hydrolysis Mechanism). Principle of Measurements. *For any kind of copolymers*, the following statistical relations between monads, dyads, and triads are applicable:

$$F_A = F_{AA} + \tfrac{1}{2}F_{\overline{AB}} \tag{1}$$

$$F_B = F_{BB} + \tfrac{1}{2}F_{\overline{AB}} \tag{2}$$

$$F_{AA} = F_{AAA} + \tfrac{1}{2}F_{\overline{AAB}} \tag{3}$$

$$F_{\overline{AB}} = F_{\overline{AAB}} + 2F_{BAB} = 2F_{ABA} + F_{\overline{BBA}} \tag{4}$$

$$F_{BB} = F_{BBB} + \tfrac{1}{2}F_{\overline{BBA}} \tag{5}$$

where F is the molar fraction of the sequences considered; average sequence lengths $\langle A \rangle$ and $\langle B \rangle$ are

$$\langle A \rangle = 2F_A/F_{\overline{AB}} \tag{6a}$$

$$\langle B \rangle = 2F_B/F_{\overline{AB}} \tag{6b}$$

The *alternating character* parameter Θ, defined by Ito and Yamashita[12] as

$$\Theta = F_{\overline{AB}}/2F_AF_B \tag{7}$$

is a measure of deviation from random statistics; these authors called it *block character*, but as the parameter is nearly zero for a diblock copolymer and equal to two for a perfectly alternating copolymer, it is more judicious to call it alternating character. For a perfectly random copolymer, the distribution is Bernoullian and we have $\Theta = 1$.

Relations 1–7 can be used for all copolymers obtained by reactions on polymers which generally lead to non-Markovian statistics, as shown by Klesper et al.[13]

For radical-initiated copolymers, the sequence distribution is a first-order Markov type; average acid and base sequence unit lengths can be calculated according to Schaefer's expressions:[14]

From the ionized acid peak

$$\langle A \rangle = 1 + 2F_{AAA}/F_{BAB} \tag{8a}$$

$$\langle A \rangle = 1 + F_{\overline{BAA}}/2F_{BAB} \tag{8b}$$

From the ester peak

$$\langle B \rangle = 1 + 2F_{BBB}/F_{\overline{BBA}} \tag{9a}$$

$$\langle B \rangle = 1 + F_{\overline{BBA}}/2F_{BBB} \tag{9b}$$

From the copolymerization theory

$$\langle A\rangle = (1 + 2r_Ar_By)/\{[(y - 1)^2 + 4r_Ar_By]^{1/2} - (y - 1)\} \qquad (10)$$

$$\Theta = (r_Ax + 2 + r_B/x)/(r_Ax + 1 + r_Ar_B/x) \qquad (11)$$

Values calculated by eq 10 for the average acid and base unit sequence lengths for the radical-initiated copolymers are listed in Table III for the two samples C_1 and C_3. These values are in agreement with those measured, using eq 8 and 9, from the ^{13}C NMR spectra as well as the dyad fractions calculated from triads (eq 3–5); thus the assignments made are justified. Θ values (eq 11) indicate a small tendency for the monomeric units to alternate because the maximum value ($\Theta_M = 1.2$) is reached when $F_A = 0.5$.

A purely random copolymer (Bernoullian or zero-order Markov process) corresponds to a theoretical model in which the addition probability P_A of a monomer A does not depend on the terminal unit of the chain. The molar fractions of acid and base are

$$F_A = P_A \qquad F_B = 1 - P_A$$

and the alternating character Θ value is 1. Average sequence lengths and triad fractions are known from the following relations:

$$\langle A\rangle = 2F_A/F_{\overline{AB}} = P_A/P_A(1 - P_A) = F_A/(1 - F_A)F_A \qquad (12)$$

$$F_{AAA} = F_A^3 \qquad F_{\overline{AAB}} = 2F_A^2(1 - F_A) \qquad F_{BAB} = F_A(1 - F_A)^2$$

$$F_{BBB} = (1 - F_A)^3 \qquad F_{\overline{BBA}} = 2F_A(1 - F_A)^2 \qquad F_{ABA} = F_A^2(1 - F_A)$$

Values of dyad and triad fractions, average sequence lengths, and values of the alternating character are listed in Table III for copolymers prepared by radical-initiated copolymerization or by acidolysis or alkaline hydrolysis. In these two last cases, the Θ values are less than one, indicating a blocklike structure.

Acidolysis by Concentrated Sulfuric Acid. As F_A increases, the average sequence lengths of the acid-hydrolyzed copolymers become greater than for the radical-initiated copolymers, especially for F_A values between 0.5 and 0.8, where $\langle A\rangle$ increases by about 1.6 in relation to the theoretical curve calculated from eq 10, slightly below the curve obtained for an ideal random copolymer using eq 12 (Table III, samples C_1 and C_2). For $F_A < 0.35$ and $F_A > 0.85$, acid unit sequence lengths are of the same order for the three sets of copolymers.

Our starting polyamine is predominantly syndiotactic (% r = 74); the formation of acid block units is not so high as in the case of the hydrolysis of PMMA, for which a strong tendency toward blocking was shown by Lando et al.[15] The acid block sequences have been determined by thermally dehydrating two adjacent acid units to cyclic anhydride; the yield of anhydride is much higher than calculated for a random or an alternating distribution model. No NMR data are given. Klesper et al.[16] have reported that the acidolysis of highly syndiotactic PMMA is a random process although triad concentrations determined for the hydrolyzed copolymers deviate to some extent from those calculated for a random copolymer (Figure 13 of ref 17).

These results are supported by Figure 4, where experimental molar fractions of A-centered triads of MA–DMAEM copolymers are compared with theoretical probabilities for the radical-initiated copolymers and the purely random copolymers. Triads AAA are present in larger amounts than demanded by Bernoullian and first-order Markov processes (Figure 4, top) and confirm the blocklike character of this copolymer series; on the other hand, triads BAB and, to a smaller degree, triads $\overline{AAB}$ are less abundant than for a purely random process (Figure 4, middle, bottom). The radical-initiated copolymers are slightly more alternating than the purely random process due to the difference of the reactivity ratios r_A and r_B. This difference can be seen in Figure 5, where the calculated values of the average sequence lengths $\langle A\rangle$ from relationships 6 and 10 are compared with the theoretical curves of a purely random copolymer and the terminal model.

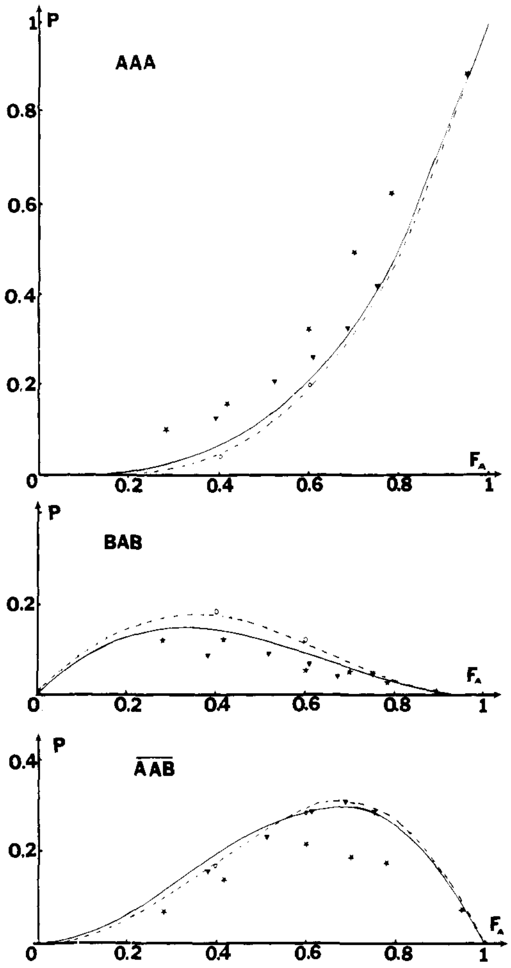

Figure 4. Experimental probabilities of A-centered triads in polyampholytes compared with theoretical curves: (——) purely random model; (– – –) terminal unit model; (★) copolymers prepared by acidolysis; (▼) copolymers prepared by alkaline hydrolysis; (○) radical-initiated copolymer.

The acidolysis of the syndiotactic polymer cannot proceed directly through the anhydride. In concentrated sulfuric acid, the exact hydrolysis mechanism is not yet known. Sulfuric acid is a strong dehydrating agent and PMA is partially dehydrated in it.[15] Acid and ester functions act as bases in this medium. The situation is quite complex because the following equilibria can exist:[18]

$$\text{RCOOR}' + \text{H}^+ \rightleftarrows \text{RCOO}^+\text{HR}' \quad \text{(fast)} \qquad (13)$$

$$\text{RCOO}^+\text{HR}' \rightleftarrows \text{RCO}^+ + \text{R}'\text{OH} \quad \text{(slow)} \qquad (14)$$

$$\text{RCO}^+ + \text{H}_2\text{SO}_4 \rightleftarrows \text{RCOO}^+\text{H}_2\text{SO}_3 \quad \text{(fast)} \qquad (15)$$

$$\text{RCOO}^+\text{H}_2\text{SO}_3 \rightleftarrows \text{RCOOSO}_3\text{H} + \text{H}^+ \quad \text{(fast)} \qquad (16)$$

The mechanism and the rate of hydrolysis of a given unit can be expected to be dependent on the nature of its neighbors. A block tendency may be favored if the aci-

Table III
Dyad and A- and B-Centered Triad Molar Fractions Measured from Figure 3, Average Sequence Lengths $\langle A\rangle$ and $\langle B\rangle$, and Alternating Character Parameter Θ Calculated from Relations 6 and 7

		dyad ratio			A-centered triad			B-centered triad					
sample	F_A	F_{AA}	$F_{\overline{AB}}$	F_{BB}	F_{AAA}	$F_{\overline{AAB}}$	F_{BAB}	F_{ABA}	$F_{\overline{BBA}}$	F_{BBB}	$\langle A\rangle$	$\langle B\rangle$	Θ
A_1	0.28	0.13	0.31	0.57	0.10	0.07	0.12	0.02	0.27	0.43	1.84	4.65	0.77
A_2	0.42	0.23	0.38	0.39	0.16	0.14	0.12	0.03	0.33	0.22	2.21	3.05	0.78
A_3	0.60	0.43	0.33	0.24	0.32	0.22	0.06	0.08	0.17	0.15	3.63	2.42	0.69
A_4	0.69	0.56	0.27	0.17	0.49	0.14	0.07	0.05	0.15	0.10	5.11	2.30	0.63
A_5	0.78	0.69	0.19	0.12	0.62	0.13	0.03	0.07	0.05	0.10	8.21	2.32	0.55
A_6	0.89	0.80	0.18	0.02	0.72	0.16	0.01	0.07	0.025	0.005	11.8	1.22	0.92
A_7	0.95	0.91	0.08	0.01	0.87	0.075	0.005	0.03	0.02	<0.005	23.75	1.25	0.84
B_1	0.38	0.21	0.34	0.45	0.13	0.16	0.09	0.09	0.16	0.37	2.23	3.65	0.72
B_2	0.52	0.32	0.40	0.28	0.21	0.23	0.09	0.08	0.24	0.16	2.60	2.40	0.80
B_3	0.61	0.40	0.42	0.18	0.26	0.28	0.07	0.14	0.14	0.11	2.90	1.86	0.88
B_4	0.67	0.48	0.39	0.13	0.32	0.31	0.04	0.14	0.11	0.08	3.43	1.69	0.88
B_5	0.75	0.56	0.37	0.07	0.42	0.28	0.05	0.15	0.07	0.03	4.05	1.35	0.99
C_1 ($f_A = 0.50$)[a]	0.40	0.14	0.52	0.34	0.02	0.12	0.20	0.12	0.29	0.19	1.53	2.30	1.08
C_3 ($f_A = 0.75$)	0.60	0.34	0.57	0.14	0.20	0.27	0.13	0.15	0.22	0.03	2.30	1.53	1.08

[a] f_A = monomeric methacrylic acid feed.

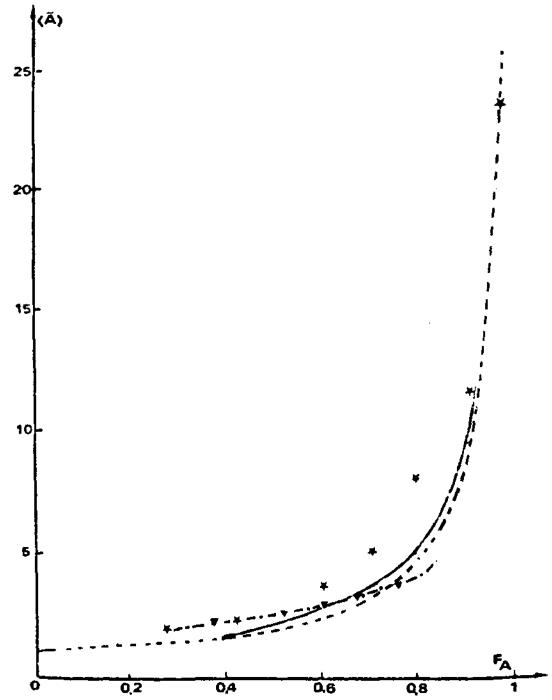

Figure 5. Average sequence length in terms of acid content F_A: (★) obtained by acidolysis; (▼) alkaline hydrolysis compared with theoretical curves; (——) purely random model; (- - -) terminal unit model.

dolysis of the amino ester is hindered by the presence of other ester units as neighbors (as in BB dyads) which could be stabilized by complexation of two amino groups by one sulfate ion. This could also be due to an inductive effect, resulting in the ionization of a neighboring amine unit which would destabilize the oxonium ion in reaction 13; when the probability of finding two or three adjacent amino ester units is very small (e.g., for $F_A > 0.8$) (Table III), this tendency should be greatly diminished.

The block tendency is seen better through the examination of the variation of the alternating character parameter Θ. Although the accuracy of the measurements of the peak areas is not very great, the alternating character parameter Θ plotted vs. F_A decreases as F_A increases up to a minimum for about $F_A \simeq 0.8$ and then increases when $F_A \rightarrow 1$ (Table III, A_1 to A_7) and this corroborates the above considerations.

In this complex situation, any detailed discussion could be fallacious. But the chemical nature of the lateral chain of the copolymer seems to be a very important factor in the blocklike tendency of copolymers prepared by acidolysis with concentrated sulfuric acid.

Alkaline Hydrolysis (KOH in Excess in 2-Propanol/Water). With a large excess of KOH (5 equiv/equiv of ester) in 2-propanol, the hydrolysis rate of PDMAEM is proportional to the reaction time and the extent of hydrolysis tends toward the limit of 75–80% after 168 h.[3] The hydrolysis is much slower than for highly syndiotactic PMMA (% A = 75 in 24 h)[19] and requires the presence of an excess of base, probably because the presence of the tertiary amino group in the AB dyads prevents the catalytic effect of the neighboring carboxylate group in the six-membered cyclic anhydride intermediate as was shown by Morawetz in the case of the PMMA alkaline hydrolysis.[20] Moreover, the backbone configuration of the chain of the polyamine (% r = 74) is not favorable to a such concerted mechanism.

The ^{13}C NMR spectra of a series of alkaline-hydrolyzed PDMAEM copolymers are shown in Figure 3B. The resolution is good enough for an evaluation of acid sequence lengths to be made (samples B in Table III) (Figure 5). The polyampholytes obtained show a weak tendency to a blocklike distribution; in the range of $0.4 < F_A < 0.8$, the acid sequence length $\langle A\rangle$ is situated between the theoretical curve for random copolymer and the curve which joins points obtained for acid-hydrolyzed copolymers; triads AAA are present in larger amounts (Figure 4), and triads BAB are present in smaller amounts than for the purely random copolymer. Nevertheless, this minor variation in sequence length is sufficient to cause differences in solubility–pH dependence (Table I).

The variation of the alternating character parameter Θ in relation to F_A gives some additional information. Θ values increase linearly with F_A when F_A is between 0.4 and 1. A greater block tendency ($\Theta < 1$) is noted in the beginning of the reaction and a tendency toward randomness ($\Theta \rightarrow 1$) is found when F_A approaches 1 (Table III, B_1 to B_5).

The variation of Θ with the progress of the reaction has not yet been investigated for postpolymerization reactions. It is different for the two kinds of hydrolysis employed in this work, and shows that the hydrolysis mechanism changes as the reaction progresses. This conclusion links up with the results of Klesper et al.[21] For alkaline hydrolysis of highly syndiotactic PMMA, these authors mention that random, blocklike, or alternating tendencies can apparently be obtained by merely changing the conditions of the polymer reaction. The hydrolysis is random if it is carried out in a dioxane/methanol/KOH mixture, a blocklike tendency is observed if the random copolymer is hydrolyzed in a second step which employs a deficient amount of aqueous KOH, and an alternating tendency is observed if the second step is carried out with an excess of aqueous KOH.[21]

These results seem to show that the ester reactivity depends to a great extent on the state of ionization of the neighboring functions and on the dielectric constant of the solvent.

Conclusion. Relation between Solubility and Sequence Distribution of Polyampholytes

Although chain microstructure has a strong effect on the physical and chemical properties of polymers, few correlations have been made until now between quantitative sequence measurements and a specific property of a copolymer. For example, the variation of glass transition temperature with copolymer composition, which was reviewed by Johnston,[22] has been explained by sequence distribution determined by ^{13}C NMR.[23]

In the field of polyampholytes, linear diblock copolymers containing cationic and anionic sequences have been synthesized by "living" anionic polymerization of 2-vinylpyridine and various methacrylates, followed by the hydrolysis of the ester sequence to free acid.[24] The range of pH values through which the polymer solution remains turbid is greater for a random copolymer than for a diblock copolymer. For our polyampholytes, the opposite is true but the pyridine group has a hydrophobic character. In 1979, Varoqui et al.[25] reported the properties of a linear diblock copolymer of a poly(styrenesulfonate)/poly(2-vinylpyridine) and suggested the formation of an internal polysalt complex of extremely compact structure to explain the considerable increase of basicity in pyridine groups of (strong acid–weak base) polyampholytes. In MA–DMAEM polyampholytes, the difference of solubility according to the method used can be explained by a greater ability of the long acid sequences to form insoluble complexes with the amine sequences and vice versa than for the random distribution chain. Significant differences are observed for the copolymers and A_3, B_3, and C_3, which have approximately the same content ($\simeq 60\%$) and which have isoelectric points at the same degree of protonation. A_3 is insoluble around the isoelectric point (pH 5.20) in pure water and the solubility range is shifted toward the acid pH in NaCl. The solubility range of B_3 remains around the isoelectric point both with and without NaCl; C_3 is soluble at all pHs in the neutralization range. Differences in triad concentration seem to be responsible for the apparent p*K*s observed, especially in high ionic strength solution, where a strengthening of the acid functions is observed for radical-initiated copolymers.[4] In this case, nearest-neighbor interactions are predominant and the nature of units around the ionizable group concerned has a major influence, in accordance with the theory of Mazur, Silberberg, and Katchalsky.[26] The largest abundance of triads $\overline{\text{AAB}}$ and BAB in this series of copolymers explains the more acidic character of the methacrylic acid units.[27]

The recent predictor–corrector method of Bauer[28] makes possible the calculation of the three relative rate constants, k_{AAA}, $k_{\overline{\text{AAB}}}$, and k_{ABA} for the two kinds of hydrolysis of the polyamine from A or B triads and it will be the subject of a future paper.

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