Microstructure of acrylamide–acrylic acid copolymers: 1. As obtained by alkaline hydrolysis

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Kinetics of alkaline hydrolysis of high molecular weight commercial polyacrylamide were studied by two different methods proposed by Fuoss and Higuchi. Compositional triad distributions and cotacticity parameters are determined from results obtained by [13]C (^{1}H) nuclear magnetic resonance of carbonyl and methine resonance patterns of partially hydrolysed polyacrylamides. It is established that acrylate monomers tend to occur as isolated groups along the molecular chain but it is not possible to assert whether there is racemization or not during the reaction.

INTRODUCTION

Poly(acrylamide-co-acrylic acid) can be obtained either by partial hydrolysis of polyacrylamide or by copolymerization of the corresponding monomers. Stimulated by the increasing interest in this class of polymers, which are one of the most used water-soluble polymers, many investigations of their properties have been reported: viscosimetric[1-3], drag-reducing[4] and flocculating properties[5]. However, a detailed comparison between the products obtained by the two different methods has never been carried out. Polymer characterization by osmometry, gel permeation chromatography and differential scanning calorimetry can afford only very indirect information about the chain microstructure[6]. Preliminary results[7] of a [13]C (^{1}H) n.m.r. study of the two polymers showed that the stability of their aqueous solutions towards Ca^{2+} depends on their preparation method and may be related to differences in the distribution of the monomer units.

The purpose of this paper is to discuss the microstructure of a series of poly(acrylamide-co-acrylic acid)s obtained by alkaline hydrolysis of polyacrylamide. In a second paper, we will present a similar study dealing with different copolymer samples.

EXPERIMENTAL

Polymer samples

Homopolymers. The sodium polyacrylate (PAA) was a polyacrylic acid sample from ICM, K & K Laboratories Inc. entirely neutralized by NaOH (molecular weight $M_w = 7 \times 10^5$). The polyacrylamide (PAM AD 10) supplied by Rhône-Poulenc Ind. was obtained by photopolymerization[8] ($M_w = 6 \times 10^6$). The low molecular weight polyacrylamide PASD Z9 was prepared in our laboratory[9] ($M_w = 2.7 \times 10^4$).

Hydrolysed polyacrylamide. The PAM AD 10 was hydrolysed by NaOH in 0.1 M NaCl aqueous solution (PAM and NaOH concentrations 0.1 and 0.25 M respectively) in a well stirred vessel and the temperature was controlled ($\pm 0.1°C$) at 30 or 50°C. At different time intervals, samples were taken from the reaction medium and the polymer was separated by precipitation in a methanol–ethanol (50/50 by volume) mixture. The polymer samples were purified by twofold precipitation and finally dried under vacuum at 40°C for at least 24 h.

Chemical characterization of the samples

Among the different methods involved in the determination of the degree of hydrolysis of polyacrylamide, τ, conductimetric or potentiometric titrations[2,3] and elemental analysis[10] have the disadvantage of being sensitive to the presence of impurities or retained water. U.v. or i.r. spectroscopy[2] allow the direct measurement of the copolymer composition but their sensitivity is not very high. In the present work, we compared the following two methods.

Potentiometric titration. The sodium acrylate–acrylamide copolymers were acidified in solution on cationic exchange resin (Class I, Merck). The acidified samples were precipitated in methanol–ethanol mixture and dried for 24 h at 40°C under vacuum.

All the titrations, by 0.01 M NaOH solutions, were performed in 0.1 M NaCl aqueous solutions of acid copolymers (concentration about 8×10^{-4} g cm^{-3}) in 2 cm^3 cells thermostated at $25 \pm 0.1°C$, under argon atmosphere. We used a Metrohm pH meter, model 605,

fitted with a microglass combined electrode (Metrohm EA 125) and an automatic microburette (Multidosimate 645). All the devices were monitored by a microcomputer (Commodore 4 032).

Data treatment was carried out according to the Wolf–Fortuin[11,12] method.

^{13}C *n.m.r. spectroscopy.* Under selected experimental conditions (see further discussion) ^{13}C n.m.r. spectroscopy can be used in a quantitative way not only for elucidation of the microstructure[13] but also for the determination of the composition[14] using the well separated resonance peaks of similar carbon atoms:

$$\tau = \frac{I_{CO}(A)}{I_{CO}(M) + I_{CO}(A)} = \frac{I_{C\alpha}(A)}{I_{C\alpha}(M) + I_{C\alpha}(A)} \quad (1)$$

where I_{CO} and $I_{C\alpha}$ are the areas of the resonance peaks of the carbonyl and the α carbon of acrylamide (M) and acrylate (A) respectively. Moreover, for all samples, the relation:

$$[I_{C\alpha}(A) + I_{C\alpha}(M)]/I_{C\beta} = 1 \quad (2)$$

(where $I_{C\beta}$ is related to the total resonance pattern of the backbone β carbon) is well satisfied. Under the analysis conditions used, differential nuclear Overhauser effects are not observed.

The τ values obtained by ^{13}C n.m.r. spectroscopy exceed those determined by potentiometry by $\sim 10\%$[15]. This difference can be explained merely by the presence in the samples of approximately 10% of retained water, which introduces an underestimation of τ by potentiometry.

In spite of their intrinsic low accuracy, the τ values derived from ^{13}C n.m.r. spectroscopy are probably the most representative of the actual copolymer composition.

Proton-decoupled ^{13}C *n.m.r. spectroscopy.* Proton-decoupled ^{13}C n.m.r. spectra were obtained within the temperature range 25–50°C, on solutions of 10 to 30% of polymer. All the hydrolysed polyacrylamides were in the form of their sodium salt in D_2O, in the presence of 1,4-dioxan as internal reference (67.40 ppm downfield from TMS). The spectrometers used in this study (Cameca 250, Cameca 350, Bruker 200) operate at 62.86, 88 and 50 MHz respectively. Flip angles and acquisition times were within the ranges 25 to 38° and 0.4 to 0.8 s respectively, the interval between the pulses being about 0.5 s.

RESULTS

Kinetics of alkaline hydrolysis of polyacrylamide

Analysis. Theoretical analysis of the kinetics and the statistics of chemical transformations of functional groups in long-chain molecules have been thoroughly discussed[16,17]. In most cases, the process can be characterized by three rate constants (k_0, k_1, k_2) for reacting groups that have 0 (I), 1 (II) and 2 (III) already modified neighbours respectively. Previous studies on the base hydrolysis of polyacrylamide have emphasized the neighbouring group effects[2,18–21] and it is firmly established that electrostatic repulsion between the anionic reagent and the polymeric substrate leads to autoretarded kinetics: $k_0 > k_1 > k_2$. Moreover, if k_2 is low

enough with respect to k_1, the reaction tends to a conversion limit.

The experimental kinetic data may be analysed according to two simplified procedures as detailed below.

Fuoss *et al.*[22] assumed that the kinetics can be represented by the following expression, α being an adjustable parameter:

$$\frac{dx}{(a-x)(b-x)} = [k_0 e^{-\alpha t} + k_n(1 - e^{-\alpha t})]dt \quad (3)$$

This is easily integrated to give:

$$F(x)/t = k_n + (k_0 - k_n)\phi(\alpha t) \quad (4)$$

with

$$\phi(\alpha t) = (1 - e^{-\alpha t})/\alpha t \quad (5)$$

and

$$F(x) = \frac{1}{a-b} \ln\left(\frac{1 - x/a}{1 - x/b}\right) \quad (6)$$

In the case of polyacrylamide hydrolysis, the symbols are a = initial concentration in NaOH, b = initial amide group concentration, x = carboxylate group concentration at time t, the hydrolysis degree τ being $\tau = x/b$. If the contribution of triads of type III to the reaction process can be neglected (early stage of the reaction or k_2 values much lower than k_1, which is precisely the case for polyacrylamide hydrolysis at 50°C), k_0 and k_1 may be obtained either by a simple graphical procedure or by numerical calculations. We determined by computer the value of the adjustable parameter α that leads to the best regression in the least-squares analysis of expression (4).

Higuchi *et al.*[20] have separately considered the early and the late stages of polyacrylamide hydrolysis. For the first reaction step, neglecting the variations of concentration of group II due to hydrolysis, they obtain, instead of relation (4), the approximate expression:

$$\ln(1 - Kx/b) = -Kk_0 at \quad (7)$$

where

$$K = 3 - 2k_1/k_0 \quad (8)$$

if NaOH is in large excess with respect to polyacrylamide. A value of K must be found that leads to a linear relationship between reaction time and $\ln(1 - Kx/b)$. By a least-squares analysis of relation (7), one may obtain the k_0 and k_1 values from the K value and from the slope of the straight line. In the late stage, assuming that all the amide groups have disappeared, the final kinetics should be simply described by:

$$\ln[1 - x/(bR_2)] = 2k_1 at \quad (9)$$

If the conversion limit R_2 of the reaction is known, it may be possible to determine k_1 from the plot of $\ln[1 - x/(bR_2)]$ as a function of time.

Results. Our kinetic results are listed in *Table 1. Figure 1* shows the linear plots of $F(x)$ *versus* $\phi(\alpha t)$, according to

Table 1 Hydrolysis of polyacrylamide

	t (min)	τ	t (min)	τ	t (min)	τ
[PAM]=0.1 M	15	0.10	90	0.27	240	0.40
[NaOH]=0.25 M	30	0.16	120	0.29	270	0.42
[NaCl]=0.1 M	45	0.19	150	0.33	300	0.44
T=50°C	60	0.23	180	0.36	330	0.45
	75	0.25	210	0.38	360	0.46

	t (min)	τ
[PAM]=0.1 M	19	0.03
[NaOH]=0.25 M	30	0.04
[NaCl]=0.1 M	45	0.05
T=30°C	60	0.07
	75	0.09

	t (min)	τ	t (min)	τ
[PAM]=0.1 M	15	0.10	180	0.30
[NaOH]=0.25 M	30	0.13	240	0.40
T=50°C	45	0.17	420	0.48
	60	0.20	1140	0.50
	120	0.26	1500	0.55
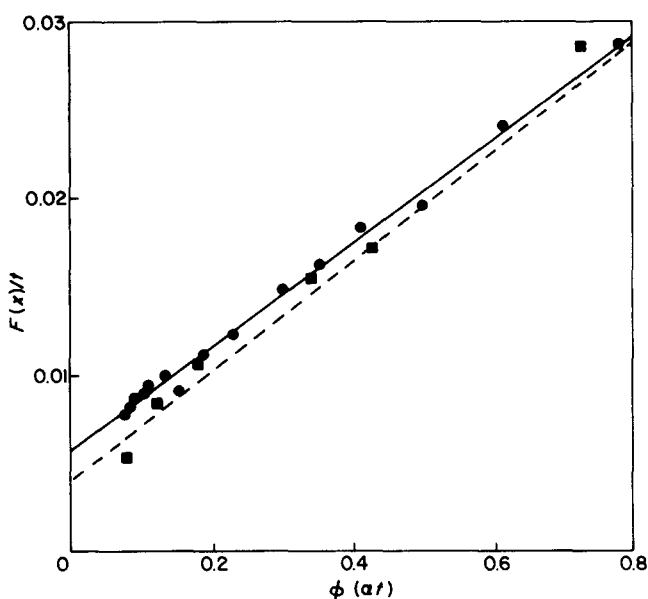
Figure 1 Plots of $F(x)/t$ versus $\phi(\alpha t)$ based on equation (4)[22]: ●, [NaOH]=0.25 M, [PAM]=0.1 M, [NaCl]=0.1 M, T=50°C; ■, [NaOH]=0.25 M, [PAM]=0.1 M, T=50°C (t in min)

relation (4), for two different experiments. The α, k_0 and k_1 values are reported in *Table 2*. We have checked that these k_0 values are equal to the initial rate constant k_i, which can be directly determined from the initial slope of $F(x)$ versus t ($k_i = 5.2 \times 10^{-4}$ l mol^{-1} s^{-1} and $k_0 = 5.8 \times 10^{-4}$ l mol^{-1} s^{-1} for hydrolysis in the presence of 0.1 M NaCl). The good linearity of the plots of *Figure 1* supports the interpretation of the hydrolysis kinetics in terms of two different rate constants k_0 and k_1. We have applied the same treatment to the experimental data of Higuchi *et al.*[20] (see *Table 3*). In *Figure 2*, where log k_0 and log k_1 are plotted versus reciprocal temperature, we observe very good agreement between the two sets of data. The ionic strength of the medium does not seem to play an important role in the early stage of the reaction, at least in the narrow range explored in these experiments (0.25–0.50 M NaCl). The k_1 values are more scattered and our results show a slight decrease of k_1 when the ionic strength

decreases. It is tempting to explain this difference by the screening of the electrostatic repulsion by the presence of NaCl salt, essentially amplified in the second rate constant k_1. This does not appear from Higuchi's experimental data, with different NaOH concentrations, and further investigations are necessary.

Although the approximations of Higuchi *et al.*[20] are valid only in the case of a pseudo-first-order reaction and in narrow ranges of time, we have applied expressions (7) and (9) to two sets of experimental data (see *Table 2*). We obtain k_0 values in good agreement with those determined from the Fuoss *et al.*[22] expressions, even for our experiments where NaOH was not in very large excess. The k_1 values are of the same order of magnitude but linear regression appears to be less good in Higuchi's expressions. Since they are based upon very rough approximations, it is reasonable to retain the k_1 values determined from Fuoss's analysis as the most reliable for this reaction.

From this kinetic study, we conclude that polyacrylamide hydrolysis is well described by the autoretarded kinetics model with three different constants. In the particular case of our experimental

Table 2 Values of α, k_0 and k_1 determined from relation (4)[a] (Fuoss *et al.*[22]) or from relations (7)[b] and (9)[c] (Higuchi *et al.*[20])

	T (°C)	α	$k_0 \times 10^4$ (l mol^{-1} s^{-1})	$k_1 \times 10^5$ (l mol^{-1} s^{-1})	k_0/k_1
This work					
[NaOH]=0.25 M,					
[PAM]=0.1 M,	50	0.036	5.8[a]	9.5[a]	6[a]
[NaCl]=0.1 M			6.02b	3.11[b]	20[b]
[NaOH]=0.25 M,					
[PAM]=0.1 M	50	0.045	6.02[a]	6.5[a]	9[a]
Higuchi *et al.*					
[NaOH]=0.25 M,	30	0.0037	1.03[a]	1.2[a]	8[a]
[PAM]=0.25 M			0.97[b]	10^{-6} [b]	
	40	0.0096	2.37[a]	3.2[a]	8[a]
			2.31[b]	11.1[b]	200[a→b]
	50	0.016	4.9[a]	3.8[a]	13[a]
			5.1[b]	1.3[b]	40[b]
[NaOH]=0.50 M,	60	0.067	15.1[a]	4.3[b→a]	36[a]
[PAM]=0.05 M				26[c]	
	70	0.091	22.8[a]	5.5[a]	41[a]
				40[c]	
	100	0.189	59.3[a]	2.51[a]	235[a]
				21.6[c]	
[NaOH]=0.50 M,	40	0.012	2.1[a]	1.1[a]	20[a]
[PAM]=0.025 M			4.3[b]	5.3[b]	8[b]

Table 3 Relative intensities and assignments of methine (peaks α, β, γ) and methylene (peaks δ, ε, ζ) (see *Figure 3*) carbon resonances for polyacrylamide (PAM AD 10) according to our hypothesis. (Apparatus Cameca 250)

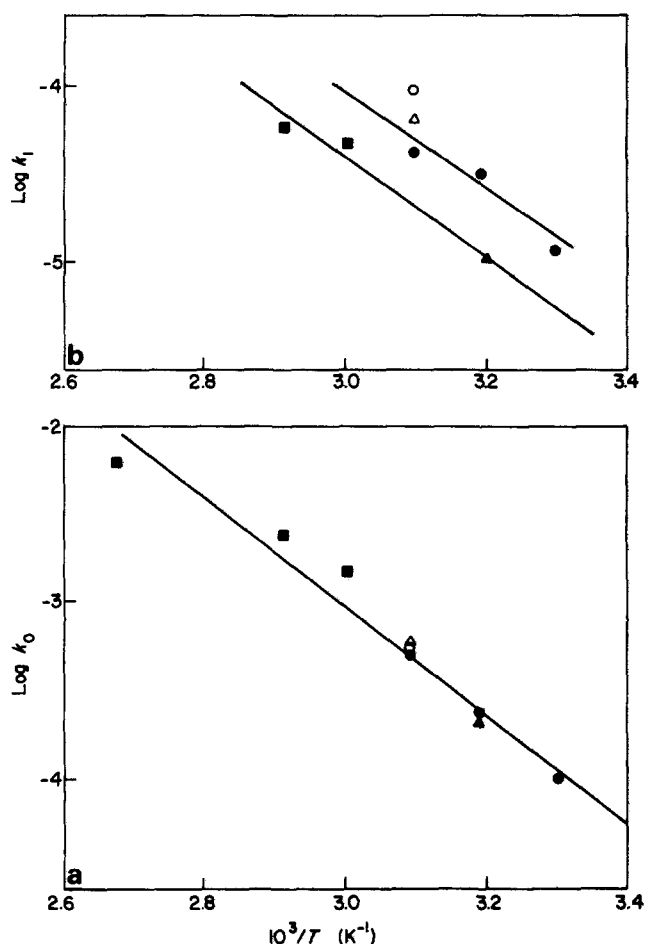| Peak	α	β	γ	δ	ε	ζ
Shift (ppm)	43.10	42.45	42.34	36.43	35.69	34.93
Tacticity assignment	(rr)	(mr+rm)(mm)		(rrr) + (mrr + rrm)	(mrm) + (rmr) + (rmm + mmr)	(mmm)
Relative intensity	0.34	0.45	0.21	0.30	0.49	0.20

Figure 2 Variations of k_0 and k_1 as a function of $1/T$. From Higuchi *et al.*[20]: ●, [NaOH] = 0.25 M, [PAM] = 0.025 M; ■, [NaOH] = 0.50 M, [PAM] = 0.05 M; ▲, [NaOH] = 0.50 M, [PAM] = 0.025 M. From this work: ○, [NaOH] = 0.25 M, [PAM] = 0.1 M, [NaCl] = 0.1 M; △, [NaOH] = 0.25 M, [PAM] = 0.1 M

conditions, the ratio k_0/k_1 is at least equal to 6 and $k_2 \sim 0$. This ratio is the main factor controlling the distribution of monomer units in the chain, and in the second part of this work we will compare [13]C n.m.r. results with theoretical predictions derived from such a value of k_0/k_1.

[13]C n.m.r. spectroscopy

Homopolymers

(1) *Polyacrylamide (PAM)*. The proton-decoupled [13]C n.m.r. spectra of PAM are given in *Figure 3* for two different molecular weights. As observed by different authors[23-26], the side-chain carbonyl carbon shows a sharp resonance without any splitting. In contrast, the methine and methylene resonances are split into three peaks, each peak resulting from partial overlap of the six possible tetrad peaks[26]. *Table 3* presents the relative areas of the three main peaks of the methine and methylene carbons. These values are in complete agreement with those found in the literature for other radically initiated polyacrylamides, although the interpretation of these spectra in terms of triad tacticity is still not definitely resolved. The lowest and highest field peaks have been assigned to the isotactic (*mm*) sequences and syndiotactic (*rr*) sequences, respectively, by Gupta *et al.*[24]. However, Lancaster *et al.*[25] have proposed the inverse assignment based on increasing syndiotacticity with decreasing polymerization temperature. For our later discussion, we will adopt this second assumption.

(2) *Poly(acrylic acid) and its sodium salt*. To our knowledge, there has been no tacticity study of poly(acrylic acid) or poly(sodium acrylate) by [13]C n.m.r. In *Figure 4* we give the n.m.r. spectra of these two polymers. The resonance peaks of the three carbons appear at lower field for the neutralized polymer and are less split than for PAM. The splitting increases in the order carbonyl < methine < methylene. In *Table 4* are reported the relative areas of the main peaks of the C_α and C_β. Our poly(acrylic acid) sample can be considered as a pure Bernoullian atactic polymer ($P_m = 0.50 \pm 0.03$) as is the case for a commercial PAA (Aldrich)[27].

Since the carbonyl resonance in homopolymers is not influenced by tacticity, for the copolymers we shall first study the corresponding peaks, which are expected to be sensitive only to compositional sequence effects. This will not be the case for C_α and C_β, which present more complex resonances due to the combined effects of tacticity and chemical environment.

Partially hydrolysed polyacrylamide

(1) *Carbonyl resonance*. *Figure 5* shows the modifications of the carbonyl resonance peak when acrylate content increases in partially hydrolysed polyacrylamides. The resonance areas of acrylamide (M), at high field, and acrylate (A), at low field, are well separated; each peak is progressively split into three lines. By following the evolution of these peaks with the copolymer composition, for the two species M and A, we have assigned each resonance of the two three-line sets to the triads $M\bar{M}M$, $M\bar{M}A$, $A\bar{M}A$ and $M\bar{A}M$, $A\bar{A}M$, $A\bar{A}A$ from the highest to the lowest field. In *Table 5* are reported the different monomer triad assignments and their relative intensity. The distribution deviates strongly from Bernoullian statistics ($k_0 = k_1 = k_2$), especially for $M\bar{M}M$
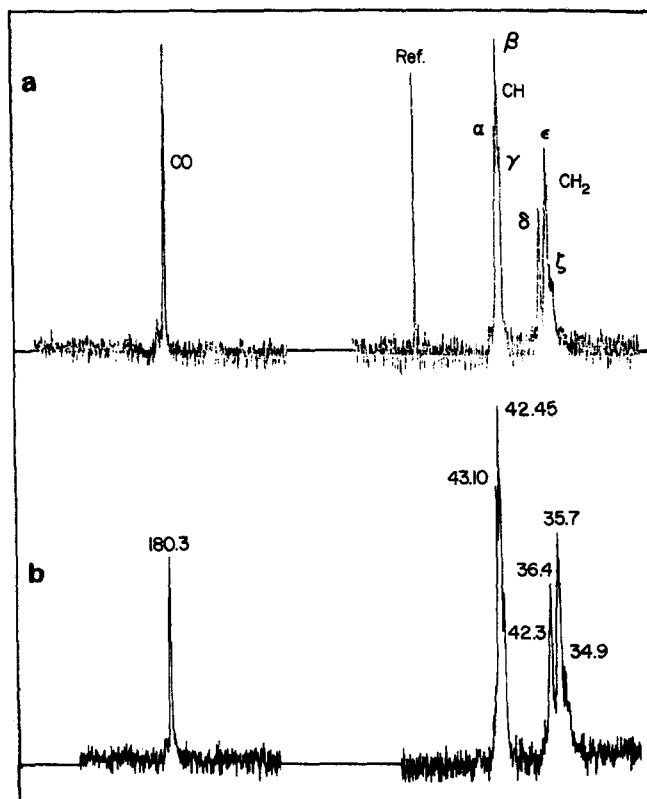

Figure 3 [13]C n.m.r. spectra of polyacrylamide samples: (a) PAM AD 10 ($\bar{M}_w = 6 \times 10^6$); (b) PASD7 Z9 ($\bar{M}_w = 2.7 \times 10^4$). (Apparatus Cameca 250)
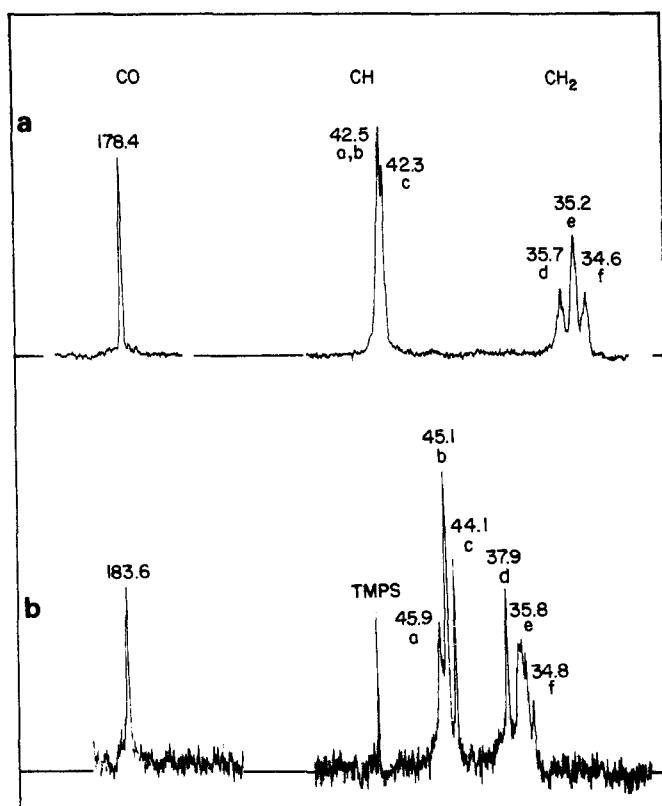
Figure 4 ^{13}C n.m.r. spectra of (a) poly(acrylic acid) and (b) poly(sodium acrylate) ($\bar{M}_w = 7 \times 10^5$). (Apparatus Cameca 250)

Table 4 Relative intensities and assignments of methine (peaks a, b, c) and methylene (peaks d, e, f) (see *Figure 4*) carbon resonances of poly(sodium acrylate). (Apparatus Cameca 250)

Peak shift (ppm)	a 45.90	b 45.10	c 44.10	d 37.90	e 35.80	f 34.80
Tacticity assignment	(rr) or (mm)	(mr + rm)	(mm) or (rr)			
Relative intensity	0.28	0.50	0.22	0.25	0.63	0.12

and AĀA triads, which are not observed even for a hydrolysis degree of 50% (see *Figure 7*).

The problem of describing the sequence length distribution from rate constants has been extensively studied by Platé *et al.*[16] and Boucher[17].

The acrylamide-centred triads, MM̄M, MM̄A and AM̄A, can be easily obtained from the different kinetic expressions proposed by Keller[28], Alfrey *et al.*[29], McQuarrie *et al.*[30], or Higuchi *et al.*[20]. Although the other approaches are based on various assumptions, they lead to numerical results which differ very slightly from those obtained by the McQuarrie relations[15]. *Figure 6* shows the very good agreement between experimental data and results calculated for $k_0/k_1 = 5$, the value determined approximately from our kinetic study.

For the calculation of acrylate-centred triads, AĀA, MĀM and MĀM, we used the approximate method proposed by Platé[16,31]. The comparison with experiment (given in *Figure 7*) is less satisfactory than for acrylamide triads, especially for MĀA. The experimental MĀM and AĀA fractions are in better agreement with the autoretarded kinetics hypothesis than with the lack-of-neighbour effect.

In a recent work, Morawetz *et al.*[32] proposed two causes of a possible deviation from predictions based on the nearest-neighbour effect:

(i) For high acrylate content of the initial polymer, the three constants k_0, k_1 and k_2 could depend on the overall polymer charge related to the dissociation of the carboxylate groups.

(ii) In basic medium, some polymer residues added head to head are changed into imide groups with a high hydrolysis rate constant.

Both effects could lead to a discrepancy between the real sequence distribution and that derived from the different models[20,28–30]. One could expect deviations of the same order of magnitude for acrylamide or acrylate triads. Moreover, Platé *et al.*[16] pointed out that the calculation of the distribution of the reacted units requires more assumptions than that of unreacted ones.

(2) *Methine and methylene carbon resonances: cotacticity study.* A complete determination of the copolymer microstructure requires us to take into account simultaneously the influence of compositional and configurational effects, combining the molar fraction F of the A and M monomers centred in the chemically different triads (already determined from the analysis of
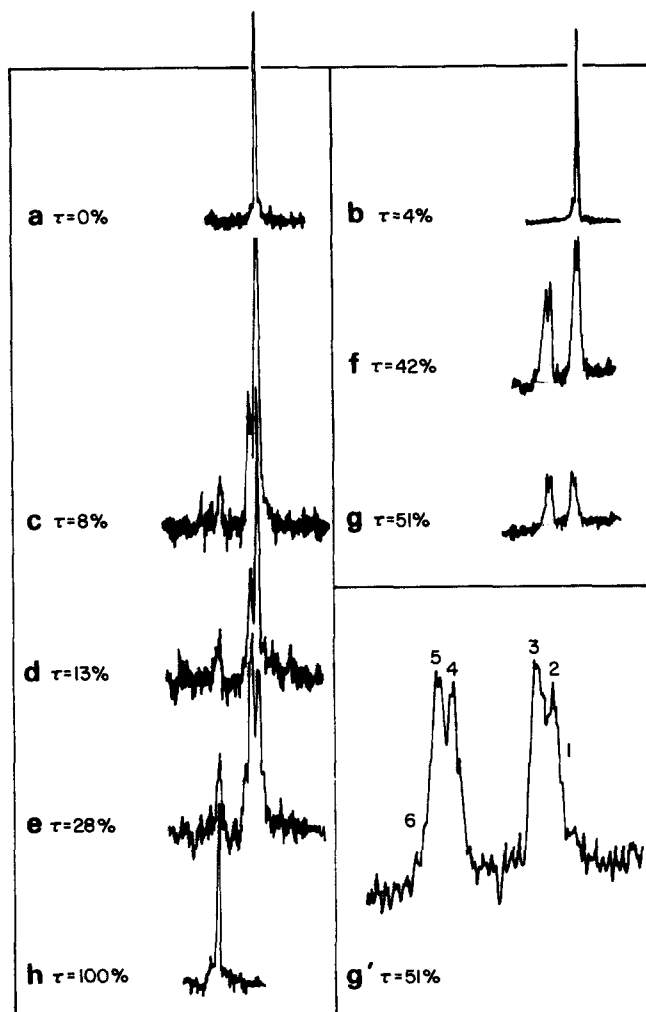

Figure 5 ^{13}C n.m.r. spectra of carbonyl resonance for a series of copolymers of various hydrolysis degrees τ. Acrylamide peak (M): (1) MM̄M, (2) MM̄A + AM̄M, (3) AM̄A. Acrylate peak (A): (4) MĀM, (5) AĀM + MĀA, (6) AĀA. (Left-hand spectra obtained with Cameca 250; right-hand spectra obtained with Cameca 350; spectrum (g′) is expanded spectrum (g))

Table 5 Relative intensities and chemical monomer triad assignments of acrylamide (M) and acrylate (A) carbonyl resonances for hydrolysed polyacrylamide (see *Figure 5*). (Apparatus Cameca 250^a, Cameca 350^b)

	M			A		
Shift (ppm)	180.30	181.06	181.50	183.60	184.01	185.10
Assignments	M$\bar{M}$M(1)	M$\bar{M}$A(2)	A$\bar{M}$A(3)	M$\bar{A}$M(4)	A$\bar{A}$M(5)	A$\bar{A}$A(6)
Relative intensities for						
H$_2$19^a (τ=0.04)	0.96	0.04	–	1	0	0
H$_2$60^a (τ=0.08)	0.82	0.18	–	1	0	0
H$_1$15^a (τ=0.13)	0.72	0.28	–	1	0	0
H$_3$90^a (τ=0.28)	0.38	0.46	0.16	0.75	0.25	0
H$_4$360^b (τ=0.42)	0.07	0.52	0.40	0.51	0.47	0.02
H$_5$9^b (τ=0.51)	0.04	0.42	0.56	0.43	0.52	0.05
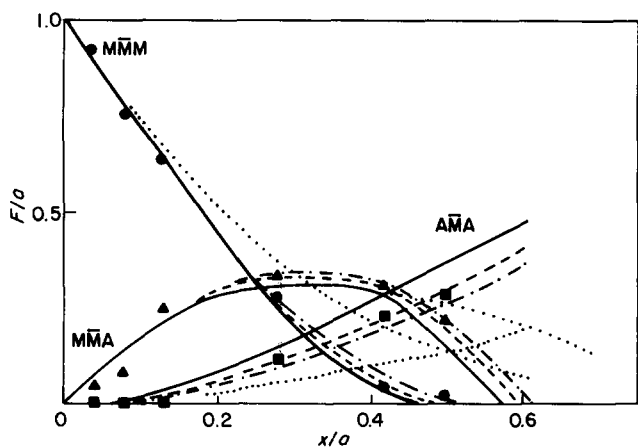
Figure 6 Variations of the different monomer triad fractions (M$\bar{M}$M, A$\bar{M}$M and A$\bar{M}$A) of acrylamide as a function of hydrolysis degree. Experimental points: ●, M$\bar{M}$M; ▲, M$\bar{M}$A+A$\bar{M}$M; ■, A$\bar{M}$A. Theoretical curves: Bernoullian statistics (·····); Higuchi's model, $k_1/k_0=0$ (————), $k_1/k_0=1/5$ (– – –), $k_1/k_0=1/3$ (–·–·–)

the carbonyl resonance data, see *Table 6*) and the various probabilities σ_{ij} of finding a meso linkage between two monomer units i and j[33,34]: see the set of equations reported in the Appendix. Taking the σ_{ij} as adjustable parameters, the sequence distribution deduced from the relations of the Appendix can be compared with that experimentally drawn from n.m.r. data. The derivation of a unique set of σ_{ij} values, which allows us to correlate all the data in a self-consistent way, and the good agreement between the σ_{MM} value and that of the polyacrylamide precursor may be considered as strong arguments in favour of correct assignment of the different n.m.r. peaks and the validity of the assumptions involved.

Peak assignment has been carried out by successive approximations, taking into account the variations of peak intensities with the copolymer composition and according to semi-empirical rules:

(i) For all the triads, the iso and syndio sequences are assumed to appear successively from the high to the low field as in the homopolymers.

(ii) The more acrylamide units in the triads, the higher will be the field at which the resonance appears.

In *Figure 8*, we have represented the resonance patterns of the methine carbon (low field) and methylene carbon (high field). As for carbonyl, the methine peaks of M (high field) and A (low field) are well resolved. As the methylene resonance patterns of A and M are partially overlapped, we shall not try to interpret them.

By using simultaneously results obtained on two series of polymers prepared by copolymerization[35], we find the
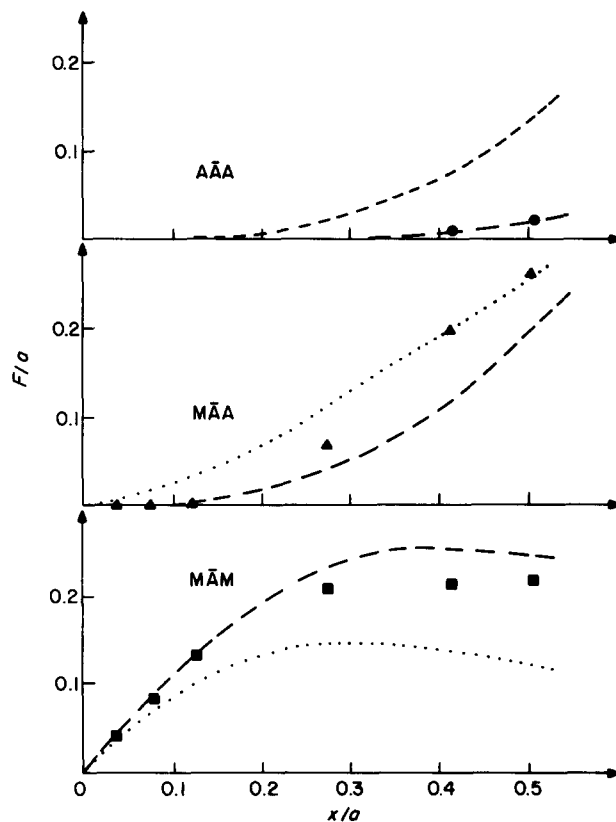

Figure 7 Variations of the monomer triad fractions (A$\bar{A}$A, A$\bar{A}$M and M$\bar{A}$M) of acrylate *versus* hydrolysis degree. Experimental points: ●, A$\bar{A}$M; ▲, A$\bar{A}$M+M$\bar{A}$A; ■, A$\bar{M}$A. Theoretical curves: Bernoullian statistics (·····); Platé relations with $k_0=1$, $k_1=0.2$, $k_2=0.01$ (– – – –)

best deconvolution of the C_α patterns to be that reported in *Table 6*.

To determine the values of the cotacticity parameters $\sigma_{AM}=\sigma$ from this set of data, we can consider two hypotheses: First, it can be assumed that the hydrolysis reaction does not modify the initial configuration of the polymer. This corresponds to $\sigma_{MM}=\sigma=\sigma_{AA}$. From the values of *Table 3* one finds $0.41<\sigma_{MM}<0.46$. Secondly, one could expect that hydrolysis leads to polymer racemization. It is known from different works[36–38] that racemization can happen in an alkaline hydrolysis if the monomer unit has a labile proton next to an electron-attracting group. This could be the case for polyacrylamide. In this hypothesis, σ_{AA} should be equal to 0.5, σ_{MM} keeping the value determined for homopolyacrylamide ($\sigma_{MM}=0.46$) and, finally, σ will be the unique adjustable parameter.

Table 6 Assignments of the C_α resonance peaks: i=iso, h=hetero, s=syndio (M, acrylamide; A, sodium acrylate)

Peak number	Chemical shift (ppm)	Assignment
(a) Acrylamide (M)		
I	42.3	$i(M\bar{M}M)$
II	42.6	$h(M\bar{M}M)+i(M\bar{M}A)$
III	43.0	$s(M\bar{M}M)+h(M\bar{M}A)$
IV	43.1	$s(M\bar{M}A)+i(A\bar{M}A)$
V	43.4	$h(A\bar{M}A)$
VI	43.8	$s(A\bar{M}A)$
(b) Sodium acrylate (A)		
1	45.2	$i(M\bar{A}M)+i(A\bar{A}M)$
2	45.6	$h(M\bar{A}M)+h(A\bar{A}M)$
3	46.2	$s(M\bar{A}M)+s(A\bar{A}M)+i(A\bar{A}A)$
4	46.8	$h(A\bar{A}A)$
5		$s(A\bar{A}A)$
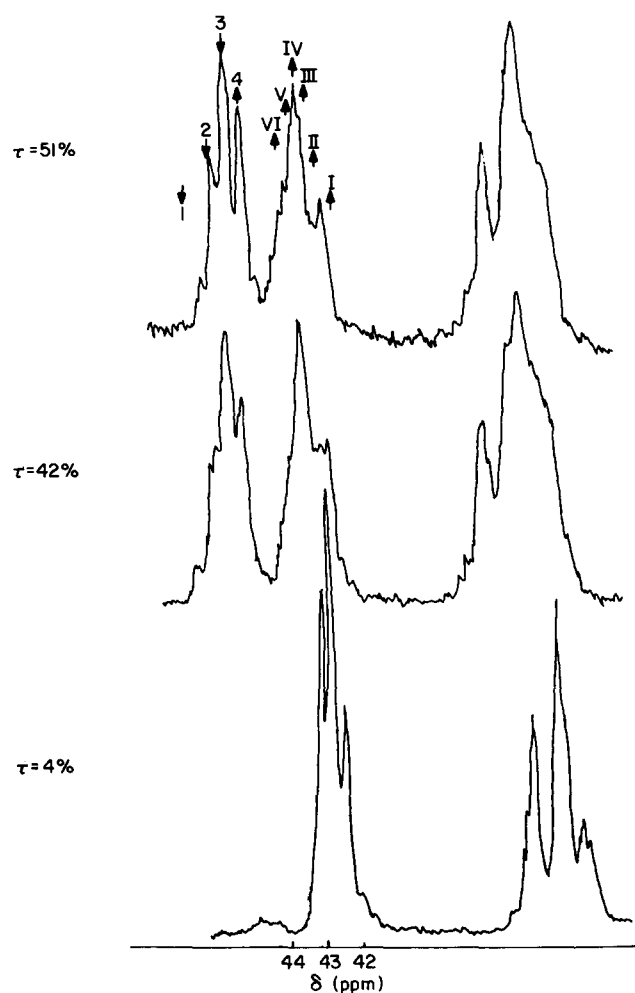
Figure 8 ^{13}C n.m.r. resonance patterns of the methine and methylene carbons for copolymers of various hydrolysis degrees. (Apparatus Cameca 250 and Cameca 350)

In *Figure 9*, we compare the experimental values of the area fractions of peaks I to VI for acrylamide with those calculated from different values of tacticity parameters, using the set of equations of the Appendix and the selected assignments given in *Table 6*. This comparison for the different peaks gives the following.

(i) Peak I ($i(M\bar{M}M)$): the best value for σ_{MM} is found to be equal to 0.46, in good agreement with the value determined for homopolyacrylamide.

(ii) Peaks V and VI ($h(A\bar{M}A)$ and $s(A\bar{M}A)$): correct agreement between calculated and experimental values is found for $0.46 < \sigma < 0.50$ (see *Figure 8*, peaks V and VI).

(iii) For all the other peaks: the experimental points are not too different from those determined by taking $\sigma_{MM}=\sigma=0.46$. Such a value is compatible with both hypotheses, racemization or no racemization.

Let us now consider the methine resonance patterns of sodium acrylate, which allow us to determine the σ_{AA} parameter. The fractions of the different co-meso triads can be calculated from a set of equations analogous to that given for acrylamide in the Appendix, the assignments reported in *Table 6* and using different values
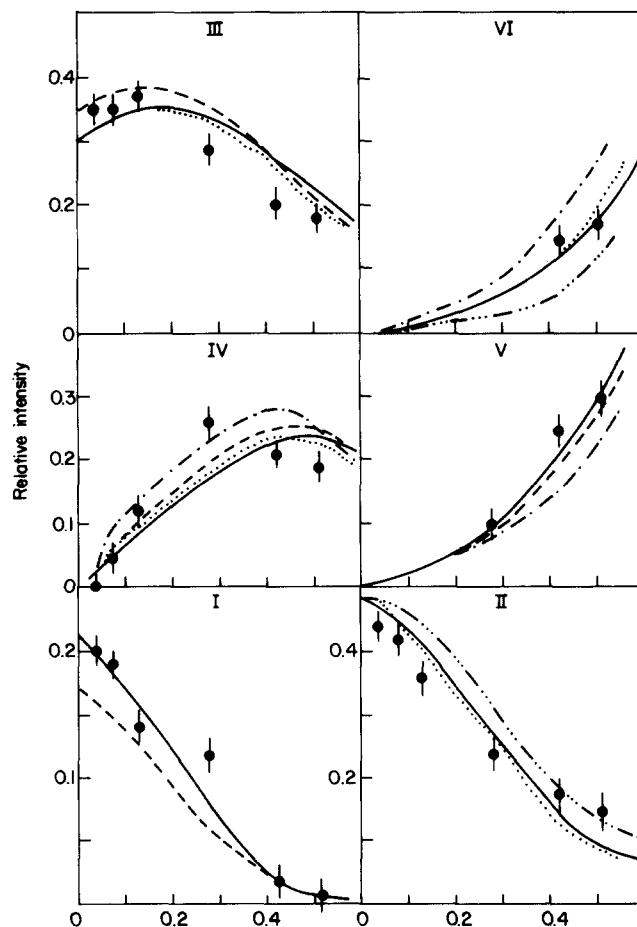

Figure 9 Experimental points and calculated curves of relative intensities of methine resonance peaks I to VI (see *Table 6*) of acrylamide units plotted as a function of hydrolysis degree. Curves calculated with $\sigma=\sigma_{MM}=0.46$ (———); $\sigma=\sigma_{MM}=0.41$ (— — —); $\sigma_{MM}=0.46$, $\sigma=0.40$ (·····); $\sigma_{MM}=0.46$, $\sigma=0.30$ (—·—·—); $\sigma_{MM}=0.46$, $\sigma=0.60$ (—·····—)

Table 7 Experimental (exp.) and calculated (1, 2, 3) values of the area fractions of different peaks of methine carbon resonances for acrylate. Values calculated with $\sigma=0.46$ and $\sigma_{AA}=0.46, 0.48, 0.50$ for (1), (2) and (3) respectively

Peak Samples	1	2	3	4	5	Method
$H_390=0.28$	0.216	0.4968	0.2916	0	0	(1)
	0.215	0.497	0.287	0	0	(2)
	0.218	0.498	0.283	0	0	(3)
	0.22	0.52	0.26	0	0	exp.
$H_4360=0.42$	0.211	0.4968	0.2916	0	0	(1)
	0.216	0.497	0.286	0	0	(2)
	0.221	0.498	0.280	0	0	(3)
	0.22	0.48	0.30	0	0	exp.
$H_59=0.51$	0.216	0.4968	0.2916	0	0	(1)
	0.217	0.4977	0.285	0	0	(2)
	0.220	0.4985	0.279	0	0	(3)
	0.20	0.50	0.29	0	0	exp.

of σ_{AA}. Experimentally only copolymers with relatively high hydrolysis degree ($\tau > 0.28$) can be studied because of the low sensitivity of the signals (proportional to τ) compared with those of polyacrylamide. For three samples, one can observe that the best agreement between experimental and calculated values is obtained for $\sigma = 0.46$ and $\sigma_{AA} = 0.50$, which should verify the second hypothesis (*Table 7*). Nevertheless, taking into account the experimental accuracy and the difference between the expected values of σ_{AA} in the two hypotheses (0.46 or 0.50), it is difficult to assert that racemization occurs in the hydrolysis of polyacrylamide.

CONCLUSION

A kinetic study of polyacrylamide hydrolysis confirms that this reaction obeys autoretarded kinetics characterized by three rate constants. The values of these constants have been determined by a rigorous treatment of our results and those of Higuchi *et al.*[20]. A well defined distribution of the monomer units in the resulting polymers is expected from such a reaction mechanism and the results of a systematic study by ^{13}C n.m.r. of hydrolysed polyacrylamide of different acrylate contents are in good agreement with the predictions. The homopolymers are essentially atactic ($\sigma_{MM} = 0.46$ for polyacrylamide and $\sigma_{AA} = 0.50$ for poly(acrylic acid)). The cotacticity parameters of the hydrolysed polymers are found to be very similar to those of homopolymers ($\sigma_{AM} = \sigma_{MA} = 0.46$). The accuracy of n.m.r. spectroscopy is not sufficient to establish whether racemization occurs during the hydrolysis reaction.

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APPENDIX

Relations between the relative fractions of the different triads and the cotacticity parameters and compositional distribution (for acrylamide)

(i = isotactic triads, h = heterotactic triads, s = syndiotactic triads)

$i(M\bar{M}M) = F_{M\bar{M}M}\sigma^2_{MM}$
$h(M\bar{M}M) = 2F_{M\bar{M}M}\sigma_{MM}(1 - \sigma_{MM})$
$s(M\bar{M}M) = F_{M\bar{M}M}(1 - \sigma_{MM})^2$

$i(M\bar{M}A + A\bar{M}M) = \frac{1}{2}F_{M\bar{M}A+A\bar{M}M}\sigma_{MM}(\sigma_{MA} + \sigma_{AM})$
$h(M\bar{M}A + A\bar{M}M) = \frac{1}{2}F_{M\bar{M}A+A\bar{M}M}\{\sigma_{MM}[(1 - \sigma_{MA})$
$\qquad\qquad + (1 - \sigma_{MM})] + (1 - \sigma_{MM})(\sigma_{MA} + \sigma_{AM})\}$
$s(M\bar{M}A + A\bar{M}M) = \frac{1}{2}F_{M\bar{M}A+A\bar{M}M}(1 - \sigma_{MM})[(1 - \sigma_{MA})$
$\qquad\qquad + (1 - \sigma_{AM})]$

$i(A\bar{M}A) = F_{A\bar{M}A}\sigma_{MA}\sigma_{AM}$
$h(A\bar{M}A) = F_{A\bar{M}A}[\sigma_{AM}(1 - \sigma_{MA}) + \sigma_{MA}(1 - \sigma_{AM})]$
$s(A\bar{M}A) = F_{A\bar{M}A}(1 - \sigma_{AM})(1 - \sigma_{MA})$

The same relations are easily obtained for acrylate.

REFERENCES

1 Klein, J. and Kulicke, W. M. *Rheol. Acta* 1976, **15**, 558
2 Muller, G., Laine, J. P. and Fenyo, J. C. *J. Polym. Sci., Polym. Chem. Edn.* 1979, **17**, 659
3 Schwartz, T. and François, J. *Makromol. Chem.* 1981, **182**, 2757
4 Ting, R. Y. and Kim, O. K. in 'Water Soluble Polymers' (Ed. N. Bikales), Plenum Press, New York, 1973
5 Nada, T., Sekiya, H. and Machi, S. *J. Appl. Polym. Sci.* 1976, **20**, 3233
6 Klein, J. and Heitzmann, R. *Makromol. Chem.* 1978, **179**, 1895
7 Truong, N. D., Galin, J. C., François, J. and Pham, Q. T. *Polym. Commun.* 1984, **24**, 208
8 Boutin, J. and Contat, J., French Patent No. 2495217, issued to Rhône-Poulenc Ind., 1980
9 Duval, M., Thesis, Strasbourg, 1982; Duval, M., François, J. and Sarazin, D. *Polymer* 1985 (in press)
10 François, J., Sarazin, D., Schwartz, T. and Weill, G. *Polymer* 1979, **20**, 969
11 Fortuin, J. M. H. *Anal. Chim. Acta* 1961, **24**, 175
12 Wolf, S. *Z. Anal. Chim.* 1970, **250**, 13
13 Randall, J. C. 'Polymer Sequence Determination, ^{13}C NMR Method', Academic Press, London, 1977
14 Zurimendi, J. A., Guerrero, S. J. and Leon, V. *Polymer* 1984, **25**, 1314
15 Truong, N. D., Thesis, Strasbourg, 1984
16 Platé, N. A. and Noah, O. V. *Adv. Polym. Sci.* 1978, **31**, 133
17 Boucher, E. A. *Prog. Polym. Sci.* 1978, **6**, 63
18 Moens, J. and Smets, G. *J. Polym. Sci.* 1957, **13**, 931
19 Nagase, K. and Sakaguchi, K. *J. Polym. Sci. A* 1965, **3**, 2475
20 Higuchi, M. and Senju, R. *Polym. J.* 1972, **3**, 370
21 Gunari, A. A. and Gundiah, S. *Makromol. Chem.* 1981, **182**, 1
22 Fuoss, R. M., Watanabe, M. and Coleman, B. D. *J. Polym. Sci.* 1960, **48**, 5
23 Cais, R. E. and Stuk, G. *J. Polymer* 1978, **19**, 179
24 Gupta, M. K. and Bansil, R. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 353
25 Lancaster, J. F. and O'Connor, M. N. *Polym. Lett.* 1982, **20**, 547
26 Inoue, Y., Fukutomi, T. and Chûjô, R. *Polym. J.* 1983, **15**, 103
27 Pham, Q. T., unpublished results
28 Keller, J. B. *J. Chem. Phys.* 1962, **37**, 2584
29 Alfrey, T. Jr and Lloyd, W. G. *J. Chem. Phys.* 1963, **38**, 318
30 McQuarrie, D. A., McTague, J. P. and Reiss, H. *Biopolymers* 1965, **3**, 657; McQuarrie, D. A. *J. Appl. Prob.* 1967, **4**, 413
31 Platé, N. A., Litmanovich, A. D., Noah, D. V., Toom, A. L. and Vasilyev, N. B. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 2165
32 Sawant, S. and Morawetz, H. *Macromolecules* 1984, **17**, 2427
33 Klesper, E. and Sielaff, G. in 'Polymer Spectroscopy' (Ed. D. O. Humme.), Verlag-Chemie, Weinheim, 1974, p. 189
34 Bovey, F. A., 'High Resolution NMR of Macromolecules', Academic Press, New York, 1972, p. 205
35 Truong, N. D., François, J., Galin, J. C. and Pham, Q. T., to be published
36 Ueno, A. and Schuerch, C. *J. Polym. Sci. B* 1965, **3**, 53
37 Matsuzaki, K., Uryu, T., Ishida, A. and Takeuchi, M. *J. Polym. Sci. C* 1967, **16**, 2099
38 Rhodes, J. H., Chiang, R. and Randall, J. C. *J. Polym. Sci. B* 1966, **4**, 393