

Microstructure of acrylamide–acrylic acid copolymers: 2. As obtained by direct copolymerization

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(Received 22 January 1985; revised 31 May 1985)

Two series of acrylamide–acrylic acid radical copolymers obtained to high conversion respectively at low and high pH were investigated by ^{13}C nuclear magnetic resonance spectroscopy. The main conclusions may be summarized as follows: (a) All copolymers are nearly atactic ($\sigma_{\text{MM}} \approx \sigma_{\text{AA}} \approx \sigma \approx 0.5$). (b) Compositional heterogeneity leads to quasi-Bernoullian distribution of acrylamide and acrylate units in spite of non-ideal reactivity ratios. (c) The presence in the copolymerization solution of Lewis acids such as ZnCl_2 or SnCl_4 does not afford alternating copolymer as claimed by Cabaness *et al.*

(Keywords: radical copolymerization; Bernoullian statistics; reactivity parameters; composition heterogeneity; ^{13}C nuclear magnetic resonance; tacticity; acrylamide; acrylic acid)

INTRODUCTION

In the previous paper¹, we have studied, using ^{13}C n.m.r. spectroscopy, the microstructure of acrylamide–acrylic acid copolymers obtained by alkaline hydrolysis of polyacrylamide. The results are in good agreement with a mechanism of autoretarded reaction, which leads to a low probability of finding long sequences of acrylate groups along the chain. Furthermore, if the reaction conversion is low enough, one can expect a very narrow composition distribution.

The same copolymers can also be obtained by copolymerization of the two corresponding monomers. It is well known that the monomer sequence distribution of copolymers is related to the reactivity ratios r_A and r_M of the monomers and depends strongly on the pH and salinity of the medium in the case of ionogenic monomers. One can also expect a compositional heterogeneity, depending on r_A and r_M values, in copolymers prepared at high conversion. To our knowledge, no systematic study has been carried out on the microstructure and monomer distribution of acrylamide–acrylic acid copolymers.

In the present work, we report the results of a ^{13}C n.m.r. study of the microstructure of two different series of samples. First, we carried out copolymerizations at low pH, where the reactivity parameters favour longer blocks of monomer units in contrast to those obtained by alkaline hydrolysis of polyacrylamide. Secondly, we studied commercial copolymers, prepared at high pH and for which this sequentiality effect must be strongly reduced.

EXPERIMENTAL

Sodium acrylate–acrylamide copolymers

Commercial samples. The copolymers AD 17, AD 27, AD 37 and AD 60 were Rhône–Poulenc samples

obtained by radical photopolymerization, in concentrated aqueous solution, at $\text{pH} > 10$ with very high degree of conversion².

Copolymerization. Acrylamide (M) (Prolabo) was twice recrystallized from acetone, and acrylic acid (A) (Prolabo) was distilled under vacuum ($P = 10^{-2}$ mmHg at 40°C) over copper turnings. Chemicals of the best reagent grade, $\text{K}_2\text{S}_2\text{O}_8$ (Merck), $\text{Na}_2\text{S}_2\text{O}_5$, ZnCl_2 and SnCl_4 (Prolabo), were used without further purification. Azobisisobutyronitrile (AIBN) (Prolabo) was recrystallized three times from benzene.

Radical copolymerization initiated by $\text{K}_2\text{S}_2\text{O}_8$ and by the redox system $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_5$ (3/2 by weight) was carried out under the following conditions: medium, pure water or 0.1 M NaCl solutions; total monomer concentration, 1 mol l^{-1} ; weight ratio initiator/monomer, 0.05; temperature, 60°C ; pH rising from 2 to 2.5 during polymerization.

Radical copolymerization initiated by AIBN in the presence of Lewis acids was carried out according to the methods described by Cabaness *et al.*^{3,4} with the following conditions: either 0.1 mol of A, M and ZnCl_2 or 0.05 mol of A, M and SnCl_4 for 50 ml of spectrophotometric-grade benzene containing 0.3 g of AIBN; temperature, 50°C ; reaction time, about 15 min.

Chemical characterization

Elemental analysis. Elemental analysis data lead to an underestimated acrylic acid content τ , if the presence of retained water or methanol and ethanol (used as precipitants) is neglected. Table 1 gives the results (for commercial copolymers) obtained by taking into account residual water. Better agreement with the potentiometric data is obtained when the elemental analyses are carried out on the acid samples.

Table 1 Acrylic acid content τ in copolymers as obtained by (1) elemental analysis (carried out on (a) acid samples or (b) sodium salt samples) (2) potentiometry, and (3) ^{13}C n.m.r. spectroscopy

Samples	τ			
	(1a)	(1b)	(2)	(3)
AD 60 (RP)	0.37 ± 0.02	0.35 ± 0.12	0.36	0.40
AD 37 (RP)	0.27 ± 0.09	–	0.22	0.24
AD 27 (RP)	0.17 ± 0.02	0.17 ± 0.10	0.17	0.17
AD 17 (RP)	0.07 ± 0.09	0.05 ± 0.05	0.07	0.07
AD 10	0.02	–	0	0
CP ₂	0.18	–	0.17	–
CP ₃	0.12	–	0.10	–
CP ₄	0.05	–	0.05	–
CPA ₂	–	–	0.36	0.40
CPA _{II}	–	–	0.43	0.50
COHPAM _I	0.05	–	0.09	–
COHPAM _{II}	0.32	–	0.27	–
CPN ₁	–	–	0.46	0.50
CPN ₃	–	–	0.16	0.18
CPN ₄	–	–	0.05	0.06
CPN ₅	–	–	0.22	0.27

Potentiometric titration. The apparatus and method have already been described in the previous paper¹.

^{13}C n.m.r. spectroscopy¹. The τ values obtained by these three methods are reported in Table 1. The data obtained by ^{13}C n.m.r. are considered as the most reliable, according to the arguments developed elsewhere^{1,5,6}.

^{13}C n.m.r. spectroscopy

Proton-decoupled ^{13}C n.m.r. spectra were obtained within the range 25–50°C, on solutions of 10 to 30% of polymer (all the copolymers are in sodium salt form) in D_2O , in the presence of 1,4-dioxane as internal reference (67.40 ppm downfield from TMS). Cameca 250, Cameca 350 and Bruker 200 spectrometers were used, operating at 62.86, 88 and 50 MHz respectively.

RESULTS AND DISCUSSION

Classical radical copolymerization

Copolymerization parameters and composition heterogeneity

(1) **Literature data.** Copolymerization parameters of acrylic acid (r_A) and acrylamide (r_M) depend on the pH^{7,8}, the ionic strength⁸ and the nature of the counterion⁹. Figure 1 shows the variations of r_A and r_M versus pH, in the absence of added salts, as obtained in three different studies^{7,8,10}. A decrease in r_A and an increase in r_M are generally observed for increasing pH. For r_A , there is rather good agreement between the different sets of values, with the exception of the data given in ref. 8 for pH 8. Although the authors explained such a result as a consequence of variations in the electrostatic repulsion with the degree of dissociation of the polymer carboxylate groups, one can consider that the curves visualized by full curves in Figure 1 represent the most probable r_A and r_M changes with pH. The r_M values of the different authors, in good agreement at low pH, deviate strongly at higher pH. From the results of Cabaness *et al.*⁷ or Bourdais¹⁰, one could expect a very high value of r_M (≥ 2) at pH 10, under which conditions the commercial samples of the AD series have been prepared. Nevertheless, it is perhaps more reasonable to use the value of 0.95 measured by Ponratnam *et al.*⁸ at pH 9.

(2) **Our experimental data (high conversion copolymerization at low pH).** Two sets of experimental copolymerization data are given in Table 2. In most cases, the reactions are carried out to high conversion ($R > 0.50$). There is normally a rather high discrepancy between the experimental values of the copolymer compositions (F) and those calculated for low conversion reactions¹¹ and using reactivity parameters reported by Cabaness⁷: $r_A = 1.73 \pm 0.21$ and $r_M = 0.49 \pm 0.06$. It is also clear that the classical Lewis–Mayo¹² or Fineman and Ross¹³ relations cannot be applied to our experiments to determine reactivity parameters.

It is well known that the instantaneous composition of a radical copolymer is a function of the composition of the monomer mixture. Skeist¹⁴, Meyer *et al.*¹⁵ and Kelen *et al.*¹⁶ have successively obtained theoretical conversion–composition relations.

We first applied the Kelen–Tüdös¹⁶ equation to determine reactivity parameters from our experimental data, limiting ourselves to copolymerizations where the reaction yield does not exceed 0.80. From this analysis, after linear regression of the η versus ξ variation, we obtain the following values for r_A and r_M :

$$r_M = 0.50 \pm 0.06 \quad (\text{see Figure 2})$$

$$r_A = 0.79 \pm 1.67$$

The accuracy of r_M is fairly good and the result is in good agreement with those reported by other authors¹⁷ at the same pH. In contrast, the lack of experimental points in the range of high acrylic acid content leads to a very low accuracy on the r_A value.

Secondly, we calculated the heterogeneity composition of our copolymers from relations giving the instantaneous copolymer composition versus the conversion rate. As shown by Shawki *et al.*⁹, it is possible to determine the copolymerization parameters by comparing the average experimental value of copolymer composition with those calculated with different pairs of r_A and r_M . On the other hand, the interpretation of ^{13}C n.m.r. results requires exact knowledge of this heterogeneity. This case is favourable for applying the analytical Meyer and Lowry expression¹⁵, which gives the conversion degree R_m as a function of the monomer feed composition f_1 , and

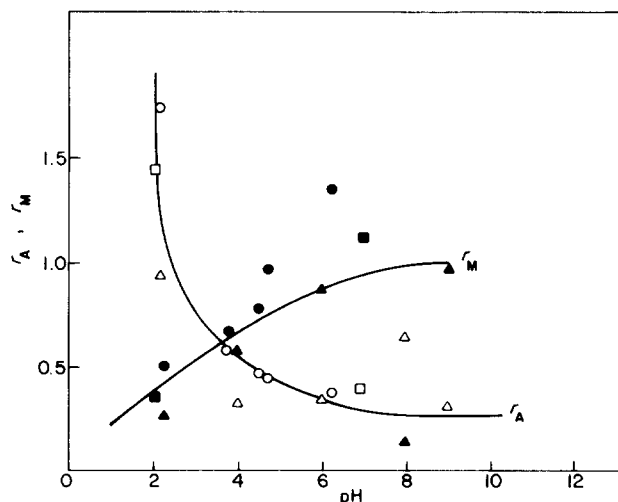


Figure 1 Variations of reactivity parameters of acrylamide r_M (full symbols) and acrylic acid r_A (open symbols) from literature data (●, ○) ref. 7; (▲, △) ref. 8; (■, □) ref. 10

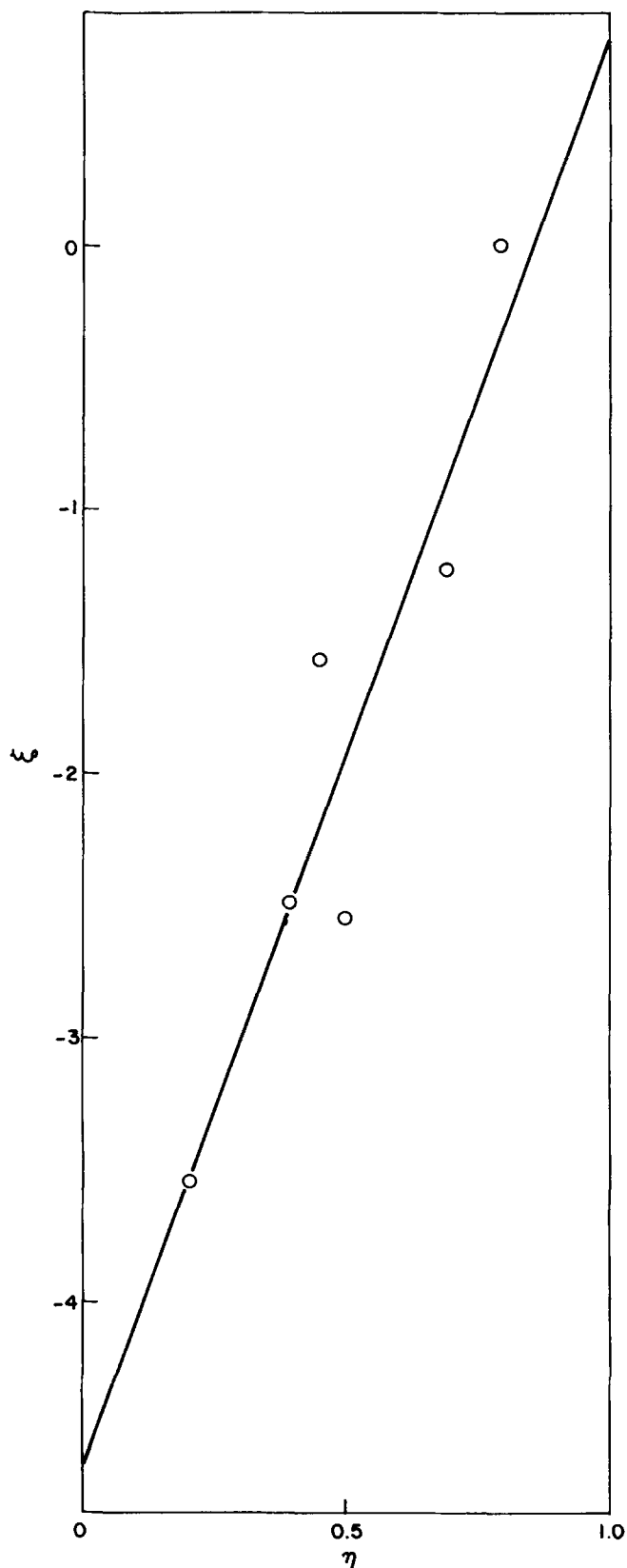


Figure 2 Plot of ξ as a function of η (Kelen-Tüdös equation¹⁶)

one can draw the variation of instantaneous content of acrylic acid in the copolymer versus R_m for two different pairs of r_A and r_M (see Figure 3). The more the r_A and r_M values differ, the higher will be the composition heterogeneity. In such pH conditions, rather homogeneous copolymers can only be obtained if R_m remains lower than 0.20.

By integrating the curves of Figure 3 between 0 and R_m , we calculated the average acrylic acid content of each of our copolymers and the values are compared in Table 2 with those determined experimentally. The good agreement between the two sets of values confirms the order of magnitude of the r_A and r_M values proposed.

(3) *High-conversion radical commercial copolymers at high pH.* The commercial copolymers (Rhône-Poulenc) are obtained² by photocopolymerization to high conversion at pH > 10. As can be seen in Figure 1, r_A and r_M values seem to remain constant for pH > 9. It is then reasonable in this case to use⁸ $r_A = 0.30$ and $r_M = 0.95$.

By assuming 100% conversion, the initial monomer composition should be equal to the final average copolymer composition and from this hypothesis we have calculated the instantaneous acrylic acid copolymer molar fraction as a function of R_m . In this case, the analytical integration of the Meyer and Lowry¹⁵ relation is not applicable ($(f_A - \delta) < 0$) and we used a numerical integral calculation by computer.

In Figure 4, we observe that there is no deviation of composition for AD 17 ($\tau = 0.07$) until a conversion of 90%, and the deviation is only 4% for AD 27 ($\tau = 0.17$), 22% for AD 37 ($\tau = 0.27$) and 36% for AD 60 ($\tau = 0.40$). In all cases, the compositional homogeneity of these copolymers could be expected to be much higher than in our copolymers, if the values of r_A and r_M used in these calculations are correct at pH 10.

¹³C (¹H) n.m.r. spectroscopy

(1) *Homopolymers.* Results on polyacrylamide, polyacrylic acid and sodium polyacrylate, all obtained by radical polymerization, have already been reported in the previous paper¹. We now recall the principal observations and conclusions.

(i) The carbonyl resonance is practically not influenced by the tacticity, whereas C_α resonances are split by configurational triad (or pentad) effects and C_β resonances by configurational hexad effects.

(ii) The assignment of tacticity triads is not yet well determined but according to our previous paper¹ we will choose the Lancaster¹⁸ and Inoue¹⁹ assignment rather

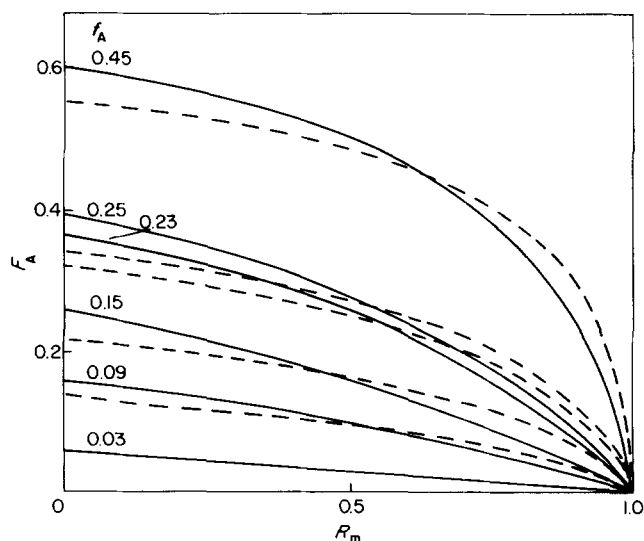


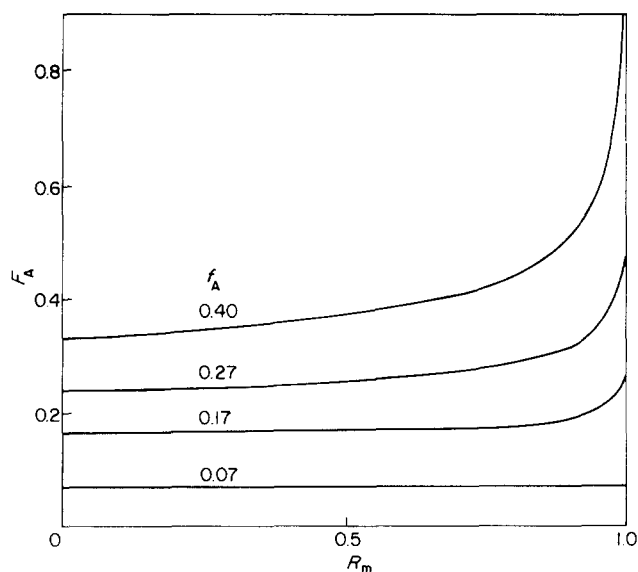
Figure 3 Instantaneous acrylic acid content of copolymers versus conversion degree (R_m) for different initial molar fractions of acrylic acid in the monomer mixtures, calculated with: $r_A = 1.73$, $r_M = 0.487$ (—); $r_A = 1.43$, $r_M = 0.60^{10}$ (---) (low pH conditions)

Table 2 Copolymerizations of acrylamide and acrylic acid (pH ~ 2–2.5). Experimental F_A (exp) and calculated F_A (calc) values of the average acrylate content F_A in copolymers: (1) obtained from Lewis-Mayo expression¹² and (2) obtained from Meyer *et al.*¹⁵ analytical expression and numerical integration, with (a) $r_A = 1.73$, $r_M = 0.49$ or (b) $r_A = 1.43$, $r_M = 0.60$

	Samples	f_A	Conversion degree	F_A (exp)	F_A (calc) (1)	F_A (calc) (2a)	F_A (calc) (2b)
[Monomers] = 1.14 M, $K_2S_2O_8$ /Monomers (g/g) = 5%, [NaCl] = 0.1 M, $T = 60^\circ C$	CP ₂	0.15	0.54	0.18	0.27	0.21	0.19
	CP ₃	0.09	0.81	0.12	0.17	0.11	0.10
	CP ₄	0.03	0.72	0.05	0.07	0.04	—
	COHPAM I ^a	0.05	0.01	0.09	0.10	—	—
	COHPAM II	0.25	0.24	0.30	0.40	0.36	0.33

^a[Monomers] = 0.1 M

	Samples	f_A	Conversion degree	F_A (exp)	F_A (calc) (1)	F_A (calc) (2a)	F_A (calc) (2b)
[Monomers] = 1 M, Initiator/Monomer (g/g) = 5%, $T = 60^\circ C$ in water	CPN ₁	0.45	0.75	0.50	0.60	0.51	0.50
	CPN ₃	0.25	0.75	0.18	0.27	0.19	0.17
	CPN ₄	0.03	0.81	0.06	0.07	0.04	—
	CPN ₅	0.23	0.81	0.27	0.37	0.26	0.25

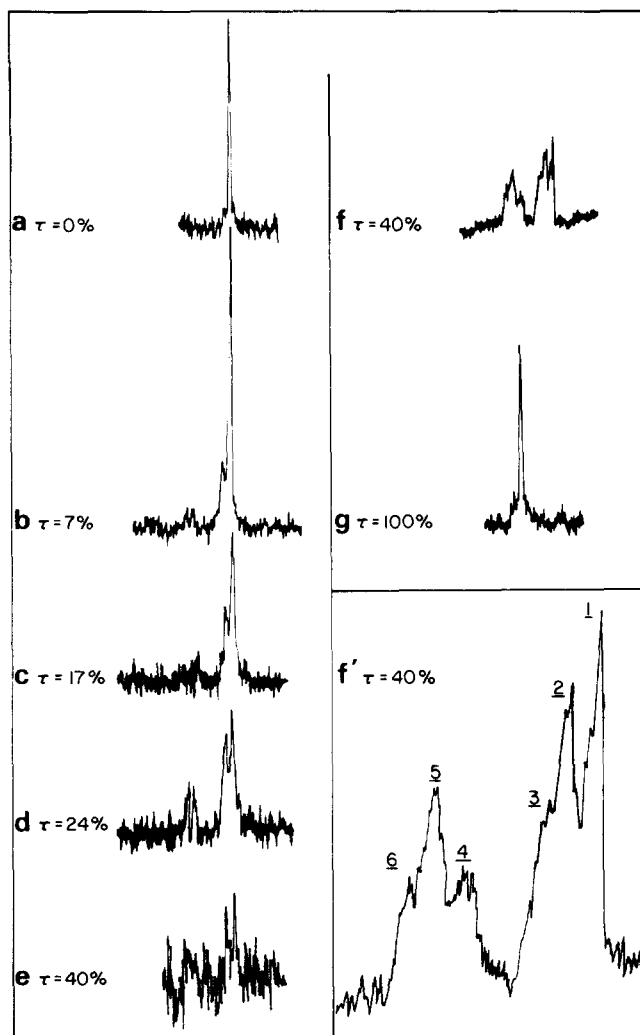

Figure 4 Molar acrylic acid content in copolymers as a function of conversion degree (R_m) for different initial molar fractions of acrylic acid, calculated with: $r_A = 0.30$, $r_M = 0.95^8$ (high pH conditions)

than that of Gupta²⁰: the low-field and high-field peaks will be assigned to the syndiotactic (rr) and isotactic (mm) triads respectively.

(iii) Tacticity parameters of the polyacrylamide (AD 10) and sodium polyacrylate (PAANa) obtained for radical polymerization are respectively determined as $\sigma_{MM} = 0.46$ at $80^\circ C$ ¹ (in agreement with the values given in ref. 18 ($\sigma_{MM} = 0.43$) and in ref. 19 ($\sigma_{MM} = 0.47$)) and $\sigma_{AA} = 0.50$.

(2) *Acrylamide-acrylic acid copolymers.* We shall successively study compositional distribution (from carbonyl resonance patterns) and cotacticity parameters (from methine carbon resonances). ¹³C n.m.r. spectra are obtained for the two previously described types of copolymers: commercial samples of high molecular weight ($M_w \sim 6 \times 10^6$) prepared at high pH (HMP), and low molecular weight samples ($100\,000 > M_w > 50\,000$) (LMP) obtained under low pH conditions.

(a) *Carbonyl resonance patterns.* Figures 5 and 6 show the evolution of carbonyl resonance peaks when acrylate content increases in acrylamide-acrylic acid copolymers,


Figure 5 ¹³C n.m.r. spectra of carbonyl resonances for a series of commercial copolymers of various acrylate content (high pH copolymerization conditions, high molecular weight of $M_w = 6 \times 10^6$). Acrylamide-centred triads (M): (1) MMM, (2) MMA + AMM, (3) AMA. Acrylate-centred triads (A): (4) MAM, (5) AAM + MAA, (6) AAA. (Left-hand spectra obtained with Cameca 250; right-hand spectra obtained with Cameca 350; spectrum (f) is expanded spectrum (g))

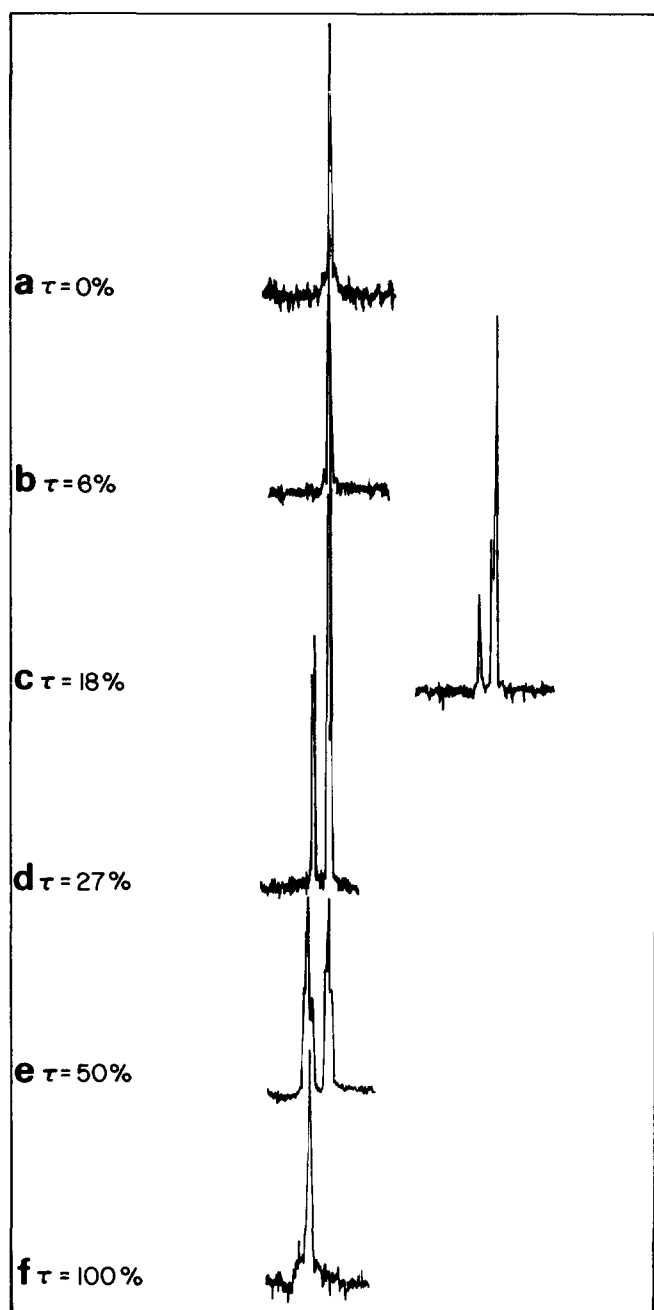


Figure 6 ^{13}C n.m.r. spectra of carbonyl resonances for a series of copolymers of various acrylate content (low pH copolymerization condition, low molecular weight of $M_w=50000$). (All spectra are obtained with Bruker 200)

for the two types HMP and LMP respectively. We can observe some differences in spectral resolution: the peaks of LMP samples are better defined compared to those of HMP especially at high acrylate content; in the latter case, a high-field apparatus (Cameca 350 at 88 MHz) is required. The resonance areas of acrylamide units (M), at high field, and acrylate units (A), at low field, are well separated and further split into two sets of three broad lines. By following the evolution of these peaks with copolymer composition, these resonances are assigned to acrylamide-centred (MMM, MMA, AMA) and acrylate-centred triads (MAM, AAM, AAA) from high to low field.

In Table 3 are reported the different chemical triad assignments and the relative intensities of each triad. Two calculations have been made for comparison with experimental data.

(i) Theoretical curves of triad distribution, for different pairs of reactivity parameters (low and high pH conditions, Bernoullian statistics), are first plotted as a function of copolymer composition in Figures 7a and b: rather good agreement is obtained between experimental points and Bernoullian statistics ($r_A=r_M=1$).

(ii) From the instantaneous copolymer composition (Figures 3 and 4) and the conversion ratio of each reaction, the average triad distribution for the two types of sample (LMP and HMP) are then also obtained for different copolymer compositions (Table 3). The agreement between experimental and calculated values is fairly good for our samples and confirms, once more, the reactivity parameter values.

The actual monomer triad distribution of AD 60 ($\tau=40\%$) strongly deviates from calculated values taking into account the drift of the monomer feed composition; longer homosequences are observed in this sample. It is worthy of note that the composition heterogeneity gives a Bernoullian distribution of monomer triads if the correct pair of reactivity ratios is used for calculations. Nevertheless, in Figure 8, the differences in the acrylamide unit distribution between acrylamide-acrylic acid copolymers obtained by alkaline hydrolysis (studied in the previous paper¹) and by copolymerization at different pH values (see theoretical curves in Figure 7) are well illustrated. Bernoullian copolymerization statistics show a less alternating monomer distribution than that obtained by an autoretarded reaction. These results seem to be in disagreement with those of Klein *et al.*²¹, who

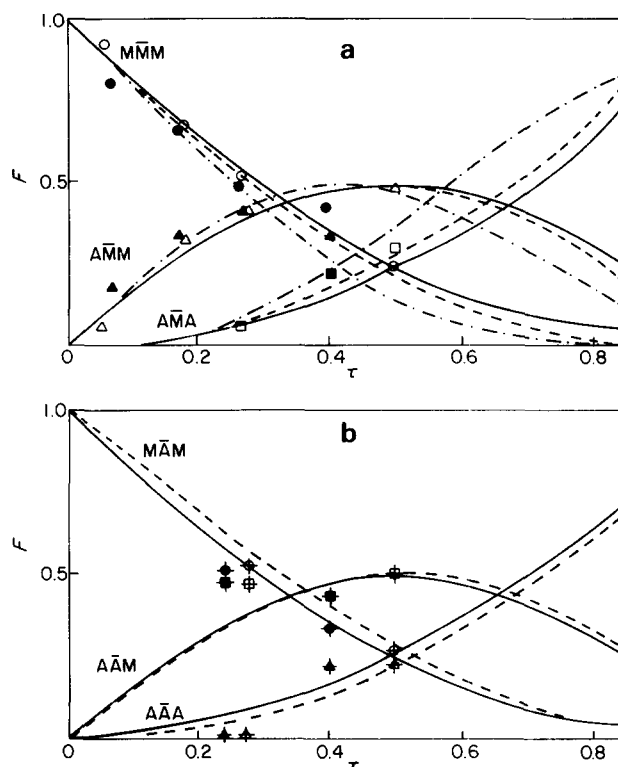


Figure 7 (a) Variations of the different acrylamide- (M) centred triad fractions versus acrylate content (τ). Experimental points: ● and ○, F_{MMM} of HMP and LMP copolymers, respectively; ▲ and △, $F_{MMA} + F_{AMM}$ of HMP and LMP; ■ and □, F_{MAM} of HMP and LMP. (b) Variations of different acrylate- (A) centred triad fractions versus acrylate content (τ). Experimental points: ● and ○, F_{MAM} of HMP and LMP, respectively; ■ and □, $F_{MAA} + F_{AAM}$ of HMP and LMP; ▲ and △, F_{AAA} of HMP and LMP. Theoretical curves in (a) and (b): Bernoullian statistics (—); calculated with $r_A=1.73$, $r_M=0.48$ (low pH) (---); $r_A=0.35$, $r_M=1.32$ (high pH) (-·-·-)

Table 3 Experimental (0, 1 or 2)^a and calculated (taking into account composition heterogeneity) chemical triad fractions from carbonyl n.m.r. data of the copolymers (AD=commercial copolymers (HMP), CPN=Laboratory copolymers (LMP)).

X-centred triad assignments	M			A			Method
	MMM(1)	MMA(2)	AMA(3)	MAM(4)	AAM(5)	AAA(6)	
Relative intensities for							
AD 17 ($\tau=0.07$)	0.81	0.18	—	—	—	—	(1)
	0.859	0.126	0.005	—	—	—	calc.
AD 27 ($\tau=0.17$)	0.65	0.35	—	—	—	—	(1)
	0.637	0.320	0.042	0.868	0.126	0.005	calc.
AD 37 ($\tau=0.24$)	0.48	0.41	0.12	0.51	0.49	—	(1)
	0.45	0.43	0.12	0.76	0.22	0.02	calc.
AD 60 ($\tau=0.40$)	0.43	0.34	0.23	0.22	0.44	0.34	(2)
	0.25	0.47	0.28	0.57	0.34	0.08	calc.
CPN ₄ ($\tau=0.06$)	0.94	0.06	—	—	—	—	(0)
	0.93	0.07	0.001	0.939	0.06	—	calc.
CPN ₃ ($\tau=0.18$)	0.67	0.33	—	—	—	—	(0)
	0.66	0.30	0.04	0.70	0.27	0.03	calc.
CPN ₅ ($\tau=0.27$)	0.52	0.42	0.06	0.53	0.47	—	(0)
	0.52	0.39	0.08	0.57	0.36	0.06	calc.
CPN ₁ ($\tau=0.50$)	0.24	0.50	0.26	0.24	0.54	0.22	(0)
	0.25	0.54	0.21	0.26	0.50	0.23	(2)
	0.21	0.49	0.21	0.26	0.49	0.25	calc.

^a(0), (1) and (2) respectively performed on Bruker 210 (50 MHz), Cameca 250 (62.86 MHz) and Cameca 350 (80 MHz) instruments

concluded that copolymerization and saponification lead to products of identical sequential distribution of monomeric units. In fact, among the different techniques used to characterize their polymers, only d.s.c. experiments may provide information about this distribution and only one sample was studied by this method.

(b) *Methine carbon resonance: cotacticity study.* For a complete determination of the copolymer microstructure, taking into account simultaneously the influence of compositional and configurational effects, one generally combines the conventional tacticity and cotacticity parameters σ_{MM} , σ_{AM} and σ_{AA} , the probability of having a meso MM, AM and AA diad^{22,23} respectively with the probability F of finding A- and M-centred triads. The compositional probability F has already been determined from carbonyl resonance data (Table 3).

To a first approximation, we will assume that $\sigma_{AM} = \sigma_{MA} = \sigma$. Taking σ , σ_{MM} and σ_{AA} as adjustable parameters, one can calculate the sequence distribution deduced from the relations of the Appendix of ref. 1 if a correct assignment of the different peaks may be found. This assignment has been carried out by successive approximations, taking into account the variations of peak intensities versus the copolymer composition and according to semi-empirical rules:

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

(ii) The more acrylamide units in a triad, the higher the field.

In Figure 9 are given the spectra of methine (low field) and methylene (high field) carbons for the two types of copolymers: those of low molecular weight (LMP) copolymers are well resolved and one can note that the methine resonance areas of acrylamide- (low field) and acrylate- (high field) centred triads are relatively well separated.

The methylene resonance presents a complex envelope (see Figure 10: expanded spectrum of AD 60 ($\tau=0.40$) recorded with Cameca 350) and an analysis was not attempted.

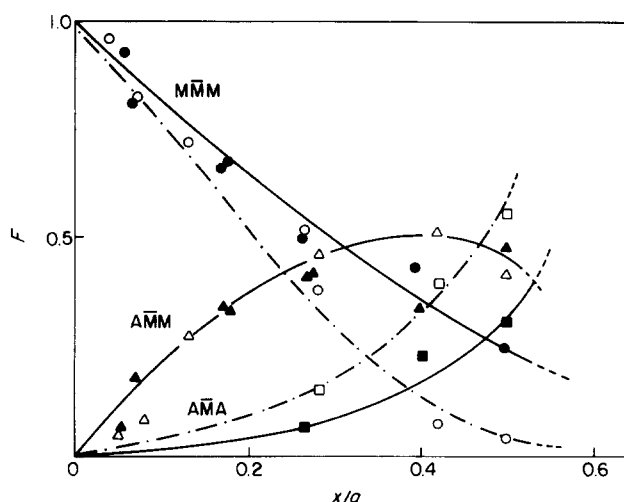


Figure 8 Variations of the different M-centred triad fractions versus acrylate content. Comparison between acrylamide–acrylic acid copolymers obtained by alkaline hydrolysis (open symbols) and copolymerization (full symbols)

The best assignments of tacticity and compositional triads to the component peaks of the methine resonance patterns are reported in Table 4. In Table 5 are given the experimental fractions of peaks I to VI for acrylamide and 1 to 5 for sodium acrylate units. Their chemical shifts are slightly higher than those published in our previous paper¹.

By using different values of the adjustable parameters σ_{MM} , σ_{AM} and σ compatible with those determined in homopolymers, it is possible to approach their values by iteration.

(1) In Figures 11 and 12, experimental and calculated data for M-centred triads are compared for different values of σ and σ_{MM} and for HMP and LMP copolymers respectively.

(i) Peak I ($i(\overline{MMM}) + i(\overline{MMA})$): the best value for σ_{MM} is found to be 0.50.

(ii) Peaks II ($h(\overline{MMM}) + h(\overline{MMA})$) and III ($s(\overline{MMM}) + s(\overline{MMA})$): these give rather good agreement with $\sigma = 0.50$ (and $\sigma_{MM} = 0.50$).

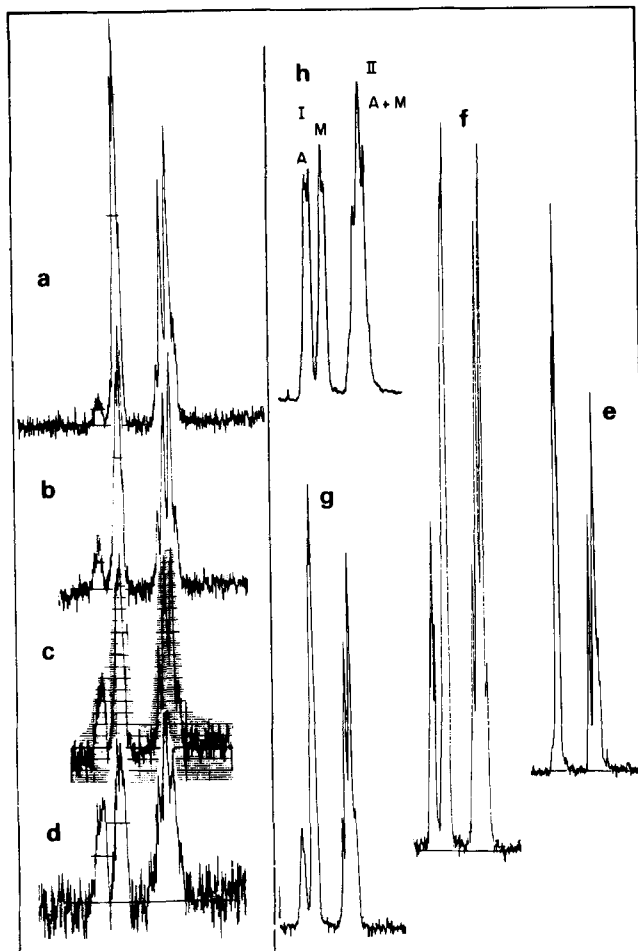


Figure 9 ^{13}C n.m.r. resonance patterns of the methine (I) and methylene (II) carbons of copolymers of various acrylate content. Spectra (a), (b), (c), (d), (Cameca 250) respectively $\tau = 0.07, 0.17, 0.24, 0.40$ (HMP). Spectra (e), (f), (g), (h), (Bruker 200) respectively $\tau = 0.06, 0.27, 0.18, 0.50$ (LMP)

(iii) Other peaks: the accuracy is so low that it is impossible to interpret them.

(2) The same calculations were performed to determine σ_{AA} (and σ) parameters for methine resonance patterns of acrylate-centred triads from equations analogous to that given for acrylamide¹ and from assignments of Table 4. Experimentally, only high acrylate content copolymers ($\tau \geq 0.24$) can be studied because of the low intensity of its resonances (proportional to τ). For the two sets of copolymers (LMP, HMP), we found the best agreement between calculated and experimental values for the values $\sigma_{AA} = 0.50$ and $\sigma = 0.50$ (Table 6). Such a result is characteristic of a Bernoullian radical copolymerization (having no penultimate effect) with negligible differences between σ_{MM} and σ_{AA} .

Radical copolymerization in the presence of Lewis acids

In order to have well defined models of sequential distribution of monomers in acrylamide-acrylic acid copolymers for n.m.r. and for many other physico-chemical studies (potentiometry, conformation, phase diagram), we have tried to prepare alternating copolymers according to the methods described by Cabaness *et al.*^{3,4}:

- 1/1: AMAMA in presence of ZnCl_2 , copolymer A
 1/4: MAAAAM in presence of SnCl_4 , copolymer B

The authors explained such a distribution by the formation of a charge-transfer intermediate complex between the donor-acceptor monomers with the Lewis acid, this complex being specific for each acid. They always found the same copolymer composition (determined by elemental analysis) whatever the monomer feed composition might be. However, the elemental analysis of our copolymers gives $\tau = 0.40$ for A and 0.50 for B, in significant disagreement with the values of 0.50 and 0.80 expected from Cabaness's conclusions.

Figures 13a and c represent the carbonyl resonance spectra of copolymers A and B (sodium salt form) respectively. Various remarks can be made:

(i) For copolymer A, one could only expect $\overline{A}MA$ and

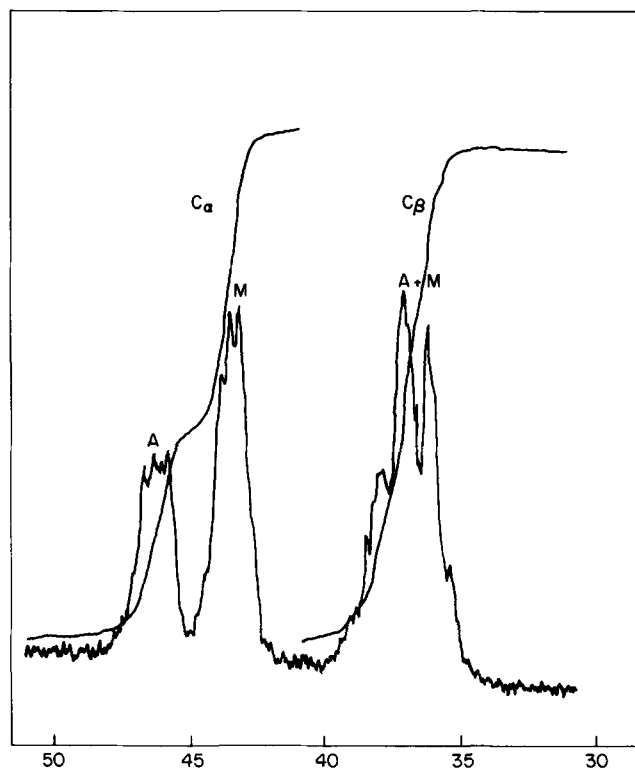


Figure 10 Expanded ^{13}C n.m.r. resonance patterns of the methine and methylene carbons of AD 60 (HMP, $\tau = 0.40$). Quantitative integration of the signals:

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

Table 4 Assignments of the methine carbon resonance peaks: *i* = iso, *h* = hetero, *s* = syndio (M, acrylamide; A, sodium acrylate)

Number of the peak	Chemical shift (ppm)	Assignment
(a) Acrylamide (M)		
I	42.4	<i>i</i> ($\overline{M}MM$)
II	43.0	<i>h</i> ($\overline{M}MM$) + <i>i</i> ($\overline{M}MA$)
III	43.3	<i>s</i> ($\overline{M}MM$) + <i>h</i> ($\overline{M}MA$)
IV	43.6	<i>s</i> ($\overline{M}MA$) + <i>i</i> ($\overline{A}MA$)
V	44.3	<i>h</i> ($\overline{A}MA$)
VI	—	<i>s</i> ($\overline{A}MA$)
(b) Sodium acrylate (A)		
1	45.5	<i>i</i> ($\overline{M}AM$) + <i>i</i> ($\overline{A}AM$)
2	45.8	<i>h</i> ($\overline{M}AM$) + <i>h</i> ($\overline{A}AM$)
3	46.0	<i>s</i> ($\overline{M}AM$) + <i>s</i> ($\overline{A}AM$) + <i>i</i> ($\overline{A}AA$)
4	46.6	<i>h</i> ($\overline{A}AA$)
5	—	<i>s</i> ($\overline{A}AA$)

Table 5 Experimental relative intensities of the different peaks decomposed from methine ^{13}C n.m.r. resonance areas of acrylamide, $C_\alpha(\text{M})$, and acrylate, $C_\alpha(\text{A})$, for the two sets of copolymers (HMP and LMP) ($C_\alpha(\text{M}) + C_\alpha(\text{A}) = 1$)

Resonance areas Shift (ppm) peak	$C_\alpha(\text{M})$				$C_\alpha(\text{A})$				
	41.3 V	43.6 IV	43.3 III	43 II	42.4 I	46.6 4	46 3	45.8 2	45.5 1
AD 10 ($\tau=0$)	0	0	0.344	0.44	0.21	0	0	0	0
AD 17 ($\tau=0.07$)	0	0.04	0.35	0.40	0.20	0	0.24	0.48	0.28
AD 27 ($\tau=0.17$)	0	0.08	0.34	0.41	0.17	0	0.21	0.43	0.30
AD 37 ($\tau=0.21$)	0	0.14	0.33	0.37	0.16	0	0.32	0.38	0.30
AD 60 ($\tau=0.40$)	0.06	0.22	0.27	0.27	0.17	0.09	0.27	0.40	0.23
CMN ₄ ($\tau=0.06$)	0	0	0.33	0.43	0.24	0	0	0	0
CPH ₃ ($\tau=0.18$)	0	0.04	0.35	0.39	0.22	0	0.26	0.48	0.26
CPH ₅ ($\tau=0.27$)	0.04	0.273	0.282	0.303	0.103	0	0.23	0.53	0.24
CPN ₁ ($\tau=0.50$)	0.09	0.32	0.290	0.246	0.05	0.14	0.25	0.36	0.24

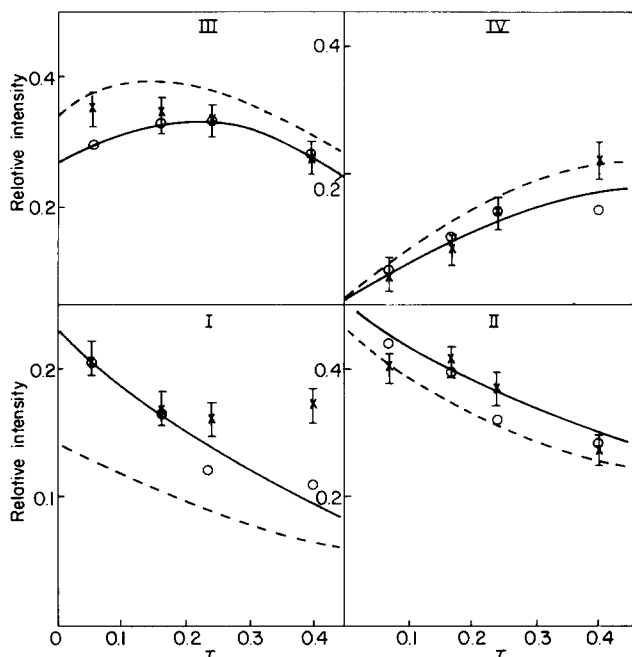
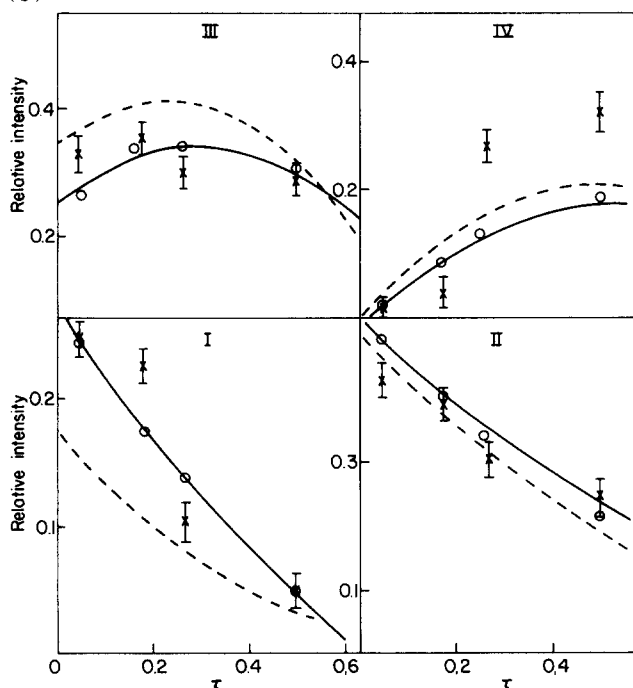

Figure 11 Experimental points (\times) and calculated curves of relative intensities of methine resonance peaks I to IV (see assignments of Table 4) of acrylamide versus acrylate content for HMP copolymers: $\sigma = \sigma_{\text{MM}} = 0.40$ (---); $\sigma = \sigma_{\text{MM}} = 0.50$ (—); $\sigma = 0.40, \sigma_{\text{MM}} = 0.50$ (○)

Figure 12 Same as Figure 11, but for LMP copolymers

Table 6 Experimental (exp.) and calculated (1, 2, 3) values of different peaks of the acrylate methine carbon resonances. Values calculated with (1) $\sigma = 0.40, \sigma_{\text{AA}} = 0.50$; (2) $\sigma = 0.46, \sigma_{\text{AA}} = 0.46$; (3) $\sigma = 0.50, \sigma_{\text{AA}} = 0.50$

Peak	1	2	3	4	5	Method
AD 37 ($\tau=0.24$)	0.18	0.49	0.33	0	0	(1)
	0.25	0.50	0.25	0	0	(3)
	0.21	0.49	0.30	0	0	(2)
	0.30	0.38	0.32	0	0	exp.
AD 60 ($\tau=0.40$)	0.14	0.38	0.31	0.11	0.05	(1)
	0.16	0.39	0.27	0.10	0.06	(2)
	0.19	0.39	0.25	0.11	0.05	(3)
	0.23	0.40	0.27	0.09		exp.
CPN ₅ ($\tau=0.27$)	0.18	0.49	0.33	0	0	(1)
	0.21	0.50	0.29			(2)
	0.25	0.50	0.25			(3)
	0.24	0.53	0.23			exp.
CPN ₁ ($\tau=0.50$)	0.14	0.37	0.30	0.11	0.06	(1)
	0.16	0.38	0.27	0.11	0.07	(2)
	0.19	0.38	0.25	0.11	0.06	(3)
	0.24	0.36	0.25	0.14	—	exp.

M $\bar{\text{A}}$ M triads without the presence of M $\bar{\text{M}}$ M, M $\bar{\text{M}}$ A + A $\bar{\text{M}}$ M, A $\bar{\text{A}}$ M + M $\bar{\text{A}}$ A and A $\bar{\text{A}}$ A triads. Actually, the spectrum in Figure 13a does not differ significantly from that of copolymer AD 60 given in Figure 5 having all the six types of triads.

(ii) For copolymer B, acrylamide should be only centred in A $\bar{\text{M}}$ A triads and acrylate in A $\bar{\text{A}}$ A or A $\bar{\text{A}}$ M. The spectrum in Figure 13c does not confirm this hypothesis.

(iii) Copolymer A was found to be very sensitive to hydrolysis in alkaline medium: with an excess of NaOH, the acrylate content increases from 0.40 to 0.70 during the n.m.r. accumulation time (8 h) at room temperature. This fact is incompatible with an alternating distribution where all the acrylamide groups have two acrylate neighbours and should consequently have a very low hydrolysis rate constant¹.

Although we have carefully applied the experimental conditions described by Cabaness *et al.*, we were not able to prepare copolymers with the distribution they predicted.

CONCLUSION

This work allows us to predict with good accuracy the sequence distribution of monomers and the compositional heterogeneity in acrylamide-acrylic acid copolymers, according to the experimental conditions used. The respective reactivities of the two monomers and high conversion lead to compounds with nearly

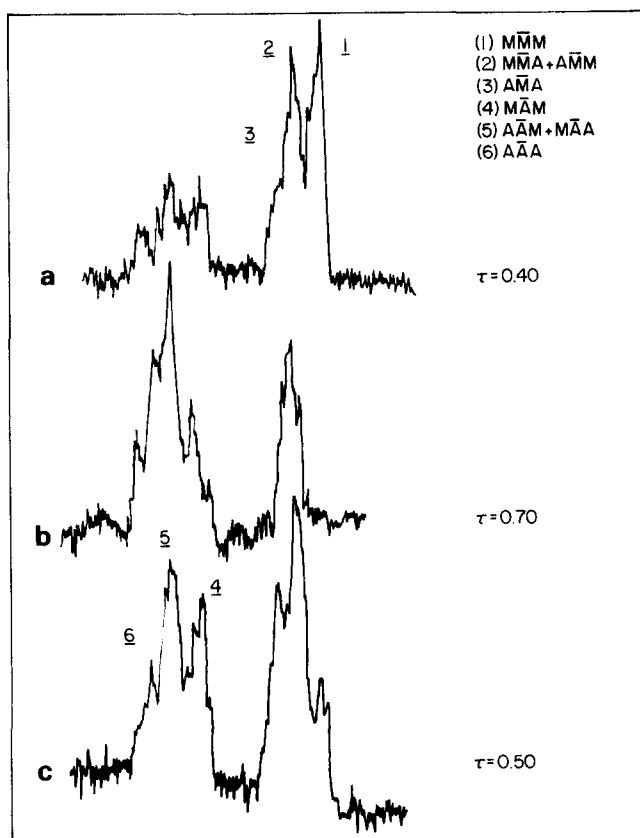


Figure 13 ^{13}C n.m.r. spectra of two radical copolymers obtained in presence of ZnCl_2 (a and b) and SnCl_4 (c)

Bernoullian statistics. The copolymerization can be carried out at higher conversion in basic medium than in acid medium if one wants to obtain homogeneous samples. But whatever the pH may be, the number average lengths of acrylamide and acrylate sequences are always higher than that found in copolymers obtained by alkaline hydrolysis. One could expect from this difference some differences in their behaviour in aqueous solution.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Professor N. Bikales for his critical reading of this work. We are indebted to Dr R. Graff for some spectra run at the Service Central de RMN, Université Louis Pasteur, Strasbourg. This research project was supported by the Ministère de la Recherche et de l'Industrie, and one of us (N. D. Truong) has benefited from a grant from the Institut Français du Pétrole.

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