European Polymer Journal, Vol. 14, pp. 109 to 116. Pergamon Press 1978. Printed in Great Britain.

ACRYLONITRILE COPOLYMERIZATION—IX.

SYNTHESIS AND CHARACTERIZATION OF COPOLYMERS WITH METHACRYLIC ACID

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(*Received* 10 *December* 1976)

Abstract—In the emulsion copolymerization of acrylonitrile (AN) with methacrylic acid (MA) at 35°, the reactivity ratios are:

$$r_{AN} = 0.128 \qquad r_{MA} = 2.40.$$

Constant composition copolymers in the range of 0–10% of methacrylic acid units have been prepared and characterized with respect to composition and sequence distribution using mostly ^1H and ^{13}C NMR spectroscopy. The observed sequence distribution from triads is Markovian first order and corresponds quite well to the computed values. The stereopropagation is nearly Bernouillian.

INTRODUCTION

In order to study the relationship between pyrolysis products, smoke production, internal cyclization reaction and sequence distribution in acrylonitrile copolymers, we chose to study acrylonitrile–methacrylic acid copolymers. According to Grassie and McGuchan [1], acidic groups introduced in polyacrylonitrile cause acceleration of the internal cyclization (nitrile groups oligomerization) through an ionic initiation mechanism. Little is known about the copolymerization of acrylonitrile (AN) and methacrylic acid (MA). Reactivity ratios for solution polymerization in ethylene glycol carbonate [2] have been given as $r_{AN} = 0.09$; $r_{MA} = 2.5$, using the method of Joshi–Kapur [3]. In this paper, we report the results of emulsion copolymerization. At first a kinetic study allowed us to derive the reactivity ratios in these conditions. Then constant composition emulsion copolymerizations were carried out and the copolymer composition and some features of the sequence distribution were calculated and partly checked through ^1H and ^{13}C NMR study.

EXPERIMENTAL

Materials

Acrylonitrile (Prolabo) was washed with NaOH 0.1 N to remove hydroquinone and then with water to neutrality. Methacrylic acid (Merck) was used without purification although it contained 0.02% hydroquinone; because of its high reactivity, it was always used in very limited amounts. Other materials (potassium persulphate, sodium metabisulphite, sodium lauroyl sulphate) were commercial products.

Polymerization conditions

The recipe contained (parts by weight): distilled water: 4 parts; monomer: 1 part; potassium persulphate: 0.001; sodium metabisulphite: 0.002; sodium lauroyl sulphate: 0.004.

Polymerization was carried out at 35° and under nitrogen (1 bar) either in batch in a 1 l. autoclave for kinetic studies or in a 5 l. autoclave with programmed addition of monomers. In both cases, the stirring speed was 750 r.p.m. (Ingenieur Bureau). The polymerization was stopped by pouring the materials into aqueous NaCl at 2–3° with stirring. The emulsion was then rapidly broken and was filtered and washed with a large excess of methanol (10 l. for 200 g of polymer). The polymer was finally dried for one day at 70° under vacuum.

Polymer characterization

An estimate of the molecular weight was obtained from viscometric measurements in dimethylformamide (DMF) at 25° using the Mark–Houwink relationship established by Onyon [4] for polyacrylonitrile.

$$(\eta) = 39.2\,10^{-3}\,M^{0.75} \text{ in ml g}^{-1}$$

The copolymer composition was determined by acid titration of a solution in DMF, using a 0.01 N aqueous NaOH with phenolphthalein as indicator. Study of the sequence distribution was carried out firstly by calculation from the reactivity ratios using a computing program initially proposed by Harwood [5] and slightly modified.

Both copolymer composition and sequence distribution were obtained from NMR HR study. We used a Varian DA 60 IL (60 MHz for ^1H) and a Varian XL 100 (25.2 MHz for ^{13}C). The polymers were dissolved (5–7% weight volume) in deuterated dimethylsulphoxide (DMSO d6) or 1–1 mixture of DMSO/DMSO d6, with HMDS and TMS as zero internal references for ^1H and ^{13}C respectively. The compositions were derived using the ^1H spectra, from the relative intensities (planimetric measurements) of the methyl resonances (1.2–1.3 ppm) of methacrylic acid units and methylene (1.7–2.3 ppm) or methine resonances (2.7–3.4 ppm) of both methacrylic acid and acrylonitrile units (Fig. 1).

RESULTS AND DISCUSSION

Reactivity ratios

A preliminary study allowed determination of the partition of the monomer into aqueous and organic phases in the polymerization conditions, except for the absence of emulsifier and redox initiator system. It was observed that the amount of AN in the

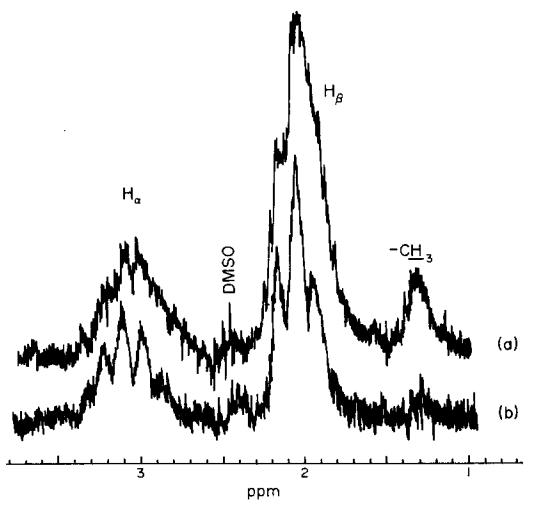

Fig. 1. ^1H – 60 MHz spectra of copolymers with 8% (a) and 3% (b) of methacrylic acid units.

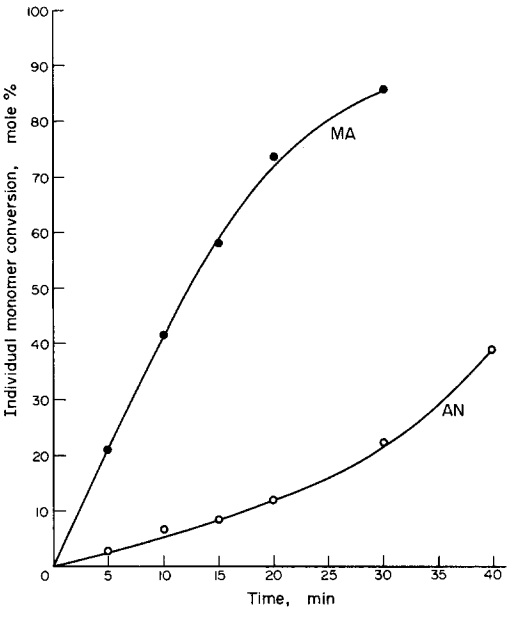

Fig. 2. Kinetic curves of acrylonitrile (0.9916 moles) and methacrylic acid (0.0084 moles) copolymerization in emulsion at 35°.

aqueous phase is between 6 and 7.5% while surprisingly almost all the MA is in the organic phase.

The results for samples taken from batch experiments after low conversion (see Table 1) show that there is a large difference between the compositions of the charge and of the copolymer. The consumption of MA is much more rapid than that of AN. So, for estimate of the initial copolymer composition, we derived the kinetic curves using gas chromatographic analysis of the monomer mixtures at various times [6]. A typical result is illustrated in Fig. 2.

For the calculation of reactivity ratios, the method of Joshi and Joshi [7] was preferred to that of Finemann–Ross. In the latter, only the r_{AN} value would be determined accurately because of the composition range used. This range was limited for two reasons. First, the reaction is too rapid to be followed kinetically by gas chromatography when the methacrylic acid content is high. Second, we were only interested in copolymers rich in acrylonitrile for our further studies of the effect of a few methacrylic acid units in the pyrolysis and combustion of acrylonitrile. The Joshi method, which is an absolute analytical process of the Mayo–Lewis plot, allows higher accuracy. One gets:

$$r_{AN} = 0.128 \pm 0.001 \qquad r_{MA} = 2.40 \pm 0.03.$$

These values are not very different from those of Simionescu *et al.* [2] for solution copolymerization at 70°.

Constant composition copolymerization

From the reactivity ratios, a program for the addition of both monomers was calculated, so that the initial feed of monomers (14.4 ± 0.1 mole) was kept constant. Since consumption of MA is much more rapid than that of AN, the addition of MA was carried out every 2.5 min instead of every 10 min for AN. The constancy of composition was checked using gas chromatography and acidimetric determination on samples taken at fixed intervals. The polymerization was stopped after 37 min. Six copolymers were prepared. For each copolymerization, the initial charge and the amounts of monomer added at fixed times are reported in Table 2. These amounts have been calculated from reactivity ratios. The results from gas chromatographic analysis are illustrated in Fig. 3, where the observed value of the ratio of the areas under the peaks of MA and AN are shown. Figure 4 shows the observed composition in the copolymer from acidimetric analysis. It may be seen that the compositions were actually kept constant with a maximum deviation of about 5%. There is no systematic drift in composition, so that it may be safely concluded that the reactivity ratios used were correct. The sampling also allowed calculation of the conversion. The results illustrated in Fig. 5 show that step I of the Smith–Ewart theory of emulsion polymerization (particle formation) is shorter when the proportion of MA increases.

After this step, it seems that the actual polymeriza-

Table 1. Batch emulsion copolymerization of acrylonitrile (AN) and methacrylic acid (MA)

Monomer feed mole		Sampling		Conversion weight,	Copolymer composition		
AN	MA	AN/MA	times, min	%	AN%	MA%	AN/MA
0.98	0.02	50	6	4.2	87.5	12.5	7
0.988	0.012	84	5	3.7	92	8	11.5
0.9916	0.0084	118	8	4.0	94	6	15.7
0.997	0.003	345	5	3.5	97.8	2.2	44.5

Table 2. Addition programs for constant composition AN–MA emulsion copolymers

Expected copolymer composition (mole % MA)	2		4		5.6		8.5		10	
Time, min	Added weight of, g MA	AN	MA	AN	MA	AN	MA	AN	MA	AN
0	3.57	759	6.62	759	10.44	759	14.66	759	18.1	759
2.5	1.3		1.7		2.1		2.0		2.5	
5	1.3		1.7		2.1		2.5		2.5	
7.5	1.5		2.0		2.3		3.0		3.0	
10	1.5	40	2.0	40	2.3	45	3.0	48	3.0	50
12.5	1.4		1.8		2.3		3.0		3.0	
15	1.4		2.0		2.4		3.5		4.0	
17.5	1.6		2.0		2.5		3.5		4.0	
20	1.7	40	2.0	40	2.4	45	3.5	48	4.0	50
22.5	1.6		2.0		2.5		3.5		4.0	
25	1.5		2.5		2.4		3.5		3.0	
27.5	1.8		2.5		2.4		3.5		5.0	
30	1.7	40	2.0	40	2.5	45	3.0	48	4.0	50
32.5	1.6		2.5		2.4		3.0		5	
35	1.6		2.5		2.5		3.0		5	

tion rate, which is mostly the rate for acrylonitrile consumption, is not dependent on the amount of methacrylic acid. It must be observed here that the acrylonitrile homopolymerization is very much slower and larger amounts of initiator are necessary (0.0086 part of potassium persulphate instead of 0.001, and 0.0172 part of sodium metabisulphite instead of 0.002). So it may be concluded that the higher polymerization rate in the presence of MA and the dependence of the first step of polymerization on the amount of MA might be explained by preferential initiation involving MA in the aqueous phase

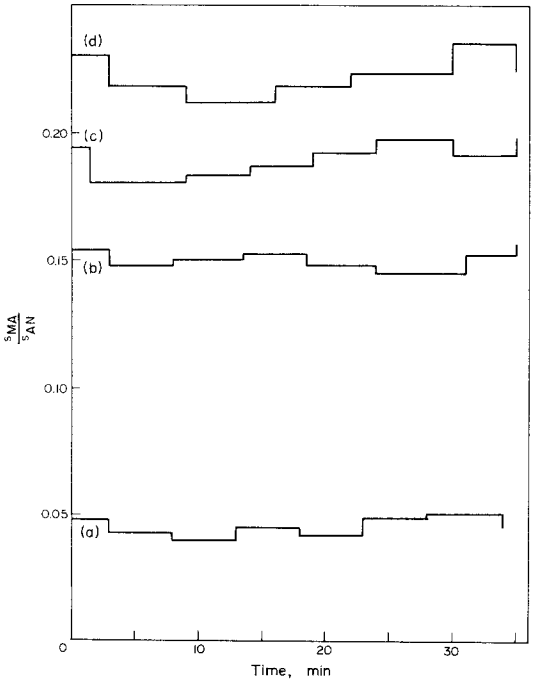

Fig. 3. Chromatographic analysis of the monomer mixture. Ratio peak areas of MA and AN S_{MA}/S_{AN} (horizontal line) vs polymerization time (vertical line) for copolymerizations with a nominal molar composition of 2% (a); 5.6% (b); 8.5% (c); 10% (d) of methacrylic acid.

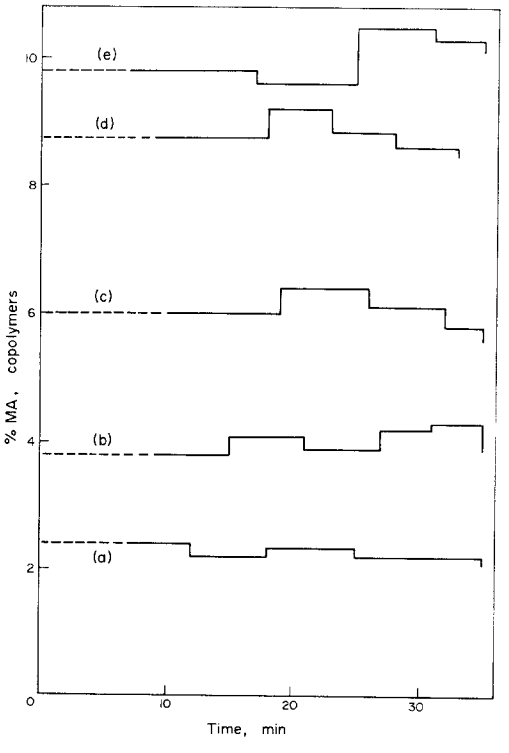

Fig. 4. Methacrylic acid contents (mole %) from acidimetric titration (horizontal line) vs polymerization time (vertical line) for copolymers with nominal molar composition of 2% (a); 4% (b); 5.6% (c); 8.5% (d) and 10% (e) of methacrylic acid.

Table 3. Constant composition acrylonitrile (AN)–methacrylic acid (MA) copolymers

Copolymer	Monomer feed mole % AN	MA	Copolymer composition Calculated from reactivity ratios AN	MA	Observed NMR AN	MA	Acid AN	MA	Viscosity* (η)	Mole weight calculated
–	100	0	100	0	100	0	100	0	494	293.000
a	99.7	0.3	97.7	2.3	97.9	2.1	97.9	2.1	760	520.000
b	99.46	0.54	95.9	4.1	95.4	4.6	96.0	4.0	882	635.000
c	99.16	0.84	94.0	6.0	94.1	5.9	94.4	5.6	962	713.000
d	98.80	1.20	91.3	8.7	89.4	10.6	91.4	8.6	808	565.000
e	98.55	1.45	90.1	9.9	91.4	8.6	89.9	10.1	924	680.000
	0	100							475	

* ml g^{-1}.

although most of the MA is present in the organic phase.

The final compositions of copolymer and results for molecular weight are reported in Table 3. The agreement between the values calculated from the reactivity ratios and observed using NMR or acidimetric titration is almost satisfactory. The molecular weights of copolymers derived using a Mark–Houwink relationship established for acrylonitrile homopolymers are of course rough estimates, although the methacrylic acid contents remain low. However, it can be seen that there are no special trends in molecular weight associated with the change in composition. It must be mentioned here that the low value for polyacrylonitrile is due to the amounts of redox initiator components were very much larger.

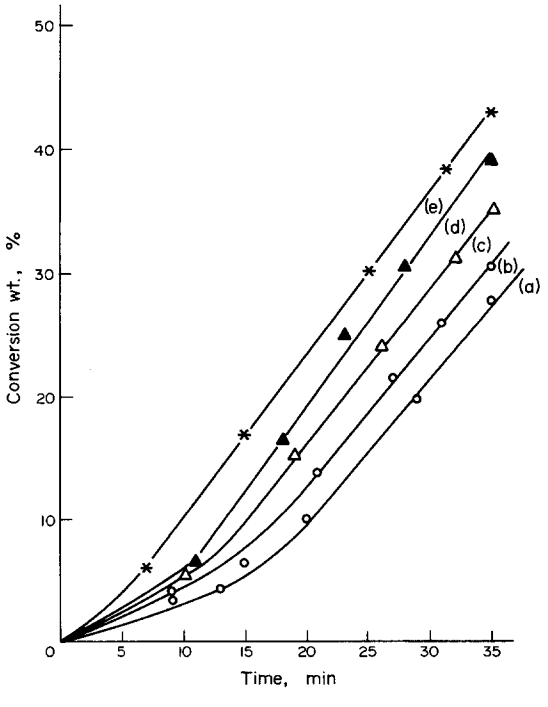

Fig. 5. Constant composition copolymerization—polymer yield from weight measurement (calculated vs the initial charge) for copolymerizations with nominal molar methacrylic acid contents of 2% (a); 4% (b); 5.6% (c); 8.5% (d) and 10% (e).

Sequence distribution

The computer program allows determination of the number average length of sequences of each unit ($L\bar{n}(A)$ for acrylonitrile, and $L\bar{n}(M)$ for methacrylic acid), the run number defined by Harwood [8] as the alternance number in 100 monomer units, the distribution function for the sequences, as well as the propagation of the different diads, triads, tetrads... Examples of these calculations are illustrated in Figs. 6–8, for the range of composition of interest for this study (0–10% methacrylic acid). The run number R_N and the average length $L\bar{n}$ (A) are in Fig. 6. The corresponding $L\bar{n}$ (M) remain close to 1 (from 1.000 to 1.036). Figure 7 shows the percent values of methacrylic acid units in diads [W_2(M)] or in triads [W_3(M)]. For the last copolymer (copolymer e in Table 3) most of the methacrylic acid units are isolated (more than 93%) and the amount of these units in sequences longer than 3 is quite negligible. Figure 8 deals with the acrylonitrile units centered in triads. In the whole range considered, most of the units are centered in homotriads, less than 20% in heterotriads and a very small amount in alternated triads.

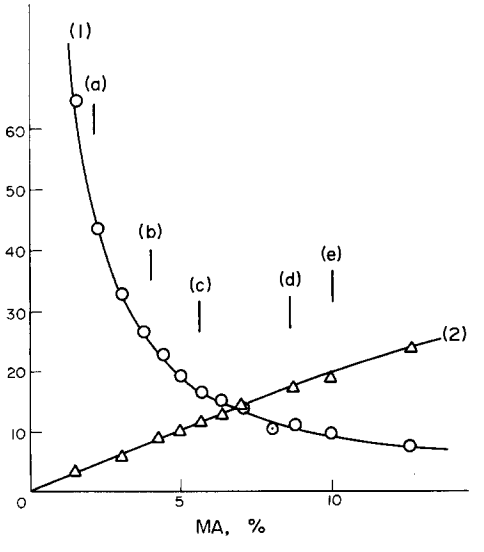

Fig. 6. Number average of acrylonitrile unit sequence length $L\bar{n}(A)$ (1) and Harwood run number (R_N) (2) as a function of the molar percent of methacrylic acid units—experimental value: ⊙.

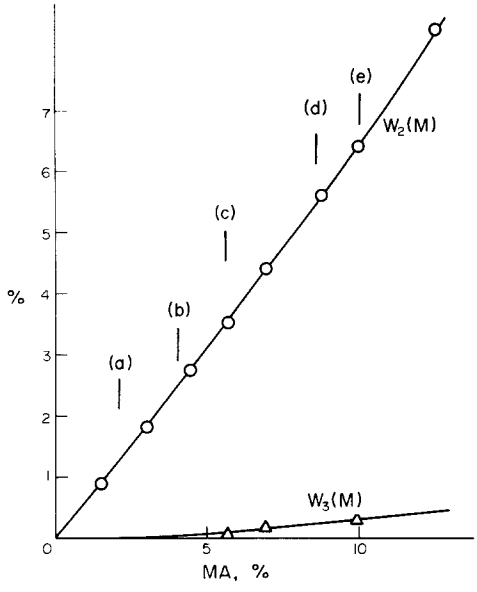

Fig. 7. Percent of the methacrylic acid units in diads: $W_2(M)$ and in triads $W_3(M)$ vs methacrylic acid units molar percent.

Some features of these calculated functions may be checked by ^{13}C NMR study. The ^{13}C NMR spectra of polyacrylonitrile have been already described [9] and the tacticity of the polymer may be studied in terms of triads using either the α-carbon atom or the nitrile group. The results are shown in Table 4 together with our results for polymethacrylic acid and

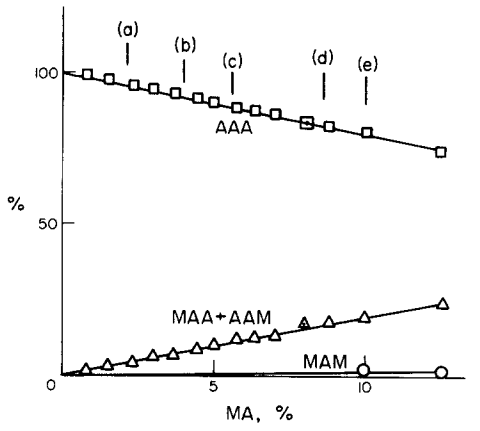

Fig. 8. Percent of acrylonitrile units centered in homotriads (A–A–A), heterotriads (△) (M–A–A) or (A–A–M) and alternated triads (M–A–M) vs methacrylic acid units molar percent—experimental values: ⊡ △.

a typical copolymer with 8% of methacrylic acid units. Some experimental points corresponding to the same copolymers are shown in Fig. 8. Again, there is a good agreement with the values calculated from the reactivity ratios. It must be noted here that NMR analysis of copolymers with too low methacrylic acid contents would not be accurate enough for a correct check of the sequence distribution. The only published examination of polymethacrylic acid is concerned with the microstructure of polymer obtained from the hydrolysis of (methyl methacrylate-methacrylic acid) copolymers [10, 11].

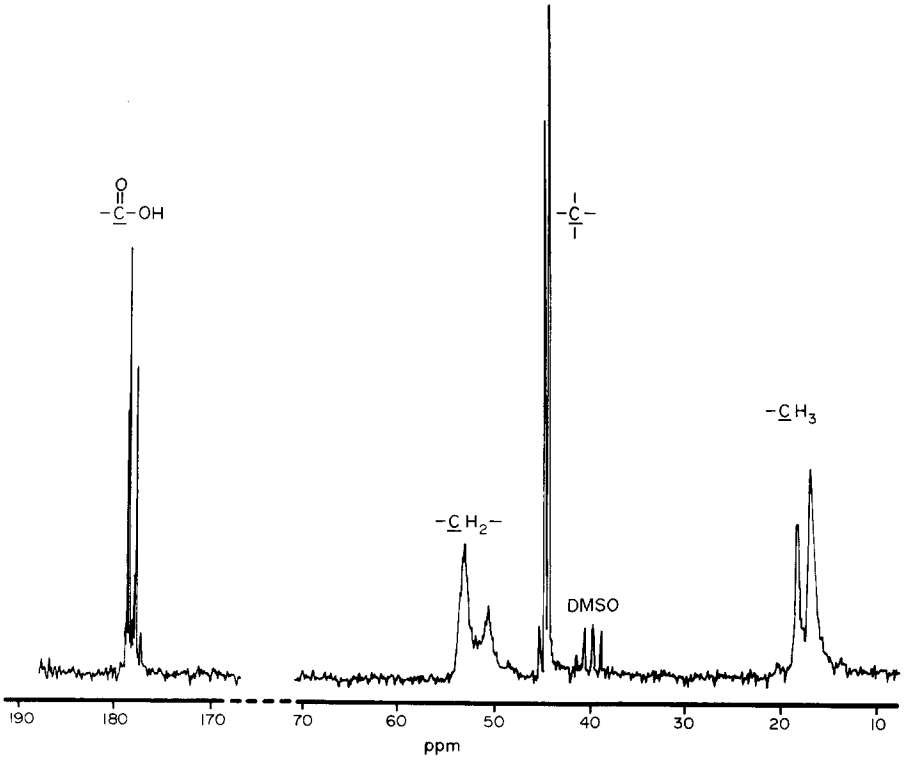

Fig. 9. ^{13}C spectrum of polymethacrylic acid in perdeuterated DMSO (99.99% D) at 140° (5500 transients).

Table 4. Triad tacticity of polyacrylonitrile (PA) polymethacrylic acid (PM) and acrylonitrile homosequences in a copolymer with 92% acrylonitrile units (PMA)

	PA			PM†			P(MA)
	Fraction	CαH (ppm)	CN (ppm)	Fraction	CH_3 (ppm)	C (ppm)	acrylonitrile sequences
mm (*i*)	0.30*	25.2	120.2	0.05	19.9	45.2	0.29
mr + *rm* (*h*)	0.48*	25.6	119.9	0.41	18.6	44.7	0.48
rr (*s*)	0.22*	26.1	119.6	0.54	16.8	44.4	0.23
m	0.54			0.25			
r	0.46			0.75			
ρ_I	1.04			1.02			
η_S	1.03			1.01			
$P(r/m) + P(m/r)$	0.97			0.98			

* Values of Ref. [8].
† With 5% of polymers in DMSO + DMSO d6 at 130–140°.

In the ^{13}C spectrum of polymethacrylic acid (Fig. 9), the triad tacticities can be calculated from the three resonance lines of both methyl and quaternary carbons. The latter are not hidden by the solvent resonances, because of the use of perdeuterated DMSO (99.99% D). Iso-, hetero-, syndiotactic triads resonate from low to high field, and their fractions are reported in Table 4. With the same polymerization conditions, polymethacrylic acid is more syndiotactic than polyacrylonitrile. In both homopolymers, the propagation statistics of the tactic triads are nearly Bernouillian.

The persistence ratios ρ_I and η_S defined respectively as [12]:

$$\rho_I = \frac{(m)(r)}{(mr)}$$

and

$$\eta_S = \frac{(rr)}{(r)^2}$$

where (m) and (r) are the proportion of meso and racemic diads and (mr) and (rr) are the proportion of heterotactic and syndiotactic triads respectively, and values of the sum $P(m/r) + P(r/m)$ are not too different from unity. Hence, one has:

$$P(m) \simeq P(m/m) \simeq P(m/r)$$

and

$$P(r) \simeq P(r/r) \simeq P(r/m).$$

$P(m)$ is the probability of the presence of meso (m) diads and $P(m/r)$ the conditional probability of a meso addition in a racemic (r) diad chain end.
One has:

$$P(m/r) = \frac{mr + rm}{2r}.$$

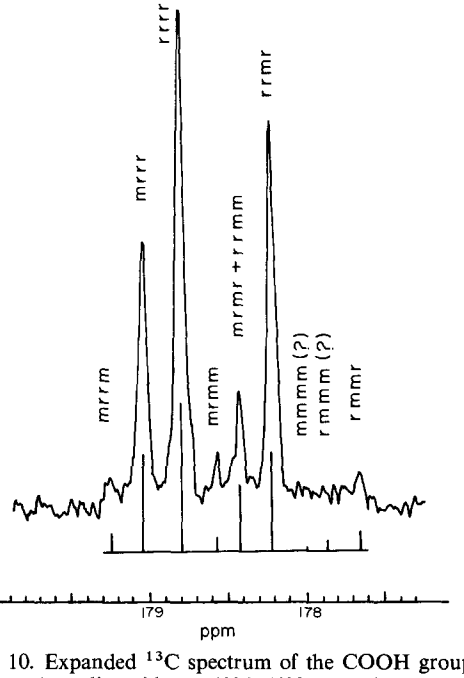

Fig. 10. Expanded ^{13}C spectrum of the COOH groups of polymethacrylic acid at 140°C (6200 transients-spectrum width: 1000 Hz) and pentad distribution. stick-spectrum: pentad relative intensities assuming Bernouillian statistics.

Table 5. Tactic pentads of polymethacrylic acid ^{13}C resonances of the COOH groups

	mrrm	*mrrr**	*rrrr*	*mrmm**	*mrmr** + *rrmr**	*rrmr**	*mmmm*	*rmmm**	*rmmr*
PPM	179.2	179.0	178.8	178.6	178.4	178.2	(178.0)	(177.9)	177.7
Observed relative intensities	0.05	0.19	0.33	0.04	0.08	0.27	(0.01)	(0.01)	0.03

* forward and reversed forms are taken into account.
(−) approximate values, weak intensities.

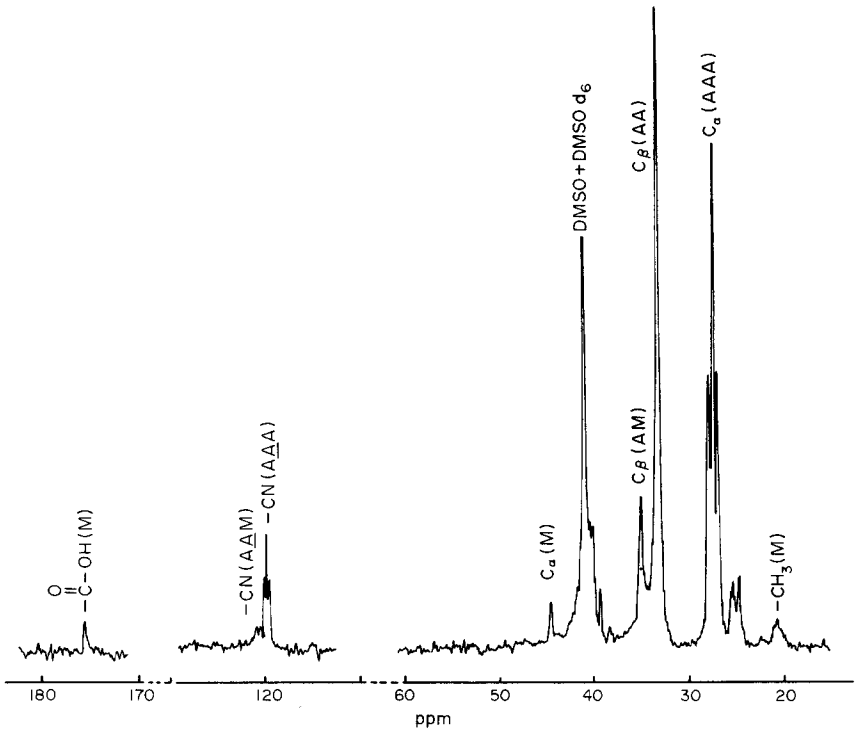

Fig. 11. ^{13}C spectrum of a copolymer with 8% methacrylic acid in DMSO + DMSO d6 (50:50) mixture at 140° (5500 transients) and attribution for diads (Cβ) and triads (Cα and CN).

If the penultimate effect concerning the possible configurational propagation is neglected, the relative intensities of the 10 diffferent pentads can be easily calculated using the experimental values of $P(m)$ and $P(r)$. The results concerning the carbon atom of the acid group are compared with the observed intensities in Table 5 and Fig. 10 (stick spectrum). The good spectral resolution obtained at 140° with a 1000 Hz spectrum width (peak width at half height = 1.75–2 Hz) allows all the lines to be resolved. Owing to the difference between the calculated and observed intensities, there should be some penultimate effect in the propagation of tactic pentads. The proposed assignment is reported in Table 5. Experimentally only 7 lines are visible, owing to the calculated intensities, the two (*mmmm*) and (*rmmm*) pentads are too weak to be recorded. This assignment differs from that of (10) and (11) for attribution of the three middle lines (Fig. 10) belonging to four pentads with centered heterotactic (*mr* or *rm*) triads.

In the ^{13}C spectrum of an acrylonitrile rich copolymer (92%) (Fig. 11) both the CO and quaternary carbon have only one resonance line (instead of nine and three respectively). An upfield shift is observed for CO (175.8 ppm) and downfield for CH_3 (21.0 ppm). It is worth noting that there are two Cβ lines easily assigned to AM or MA (35.5 ppm) and AA (33.9 ppm) diads (Fig. 9). Likewise, there are two three line resonances for CN (Fig. 12) belonging to the CN group of the A centered triads AAM or (MMA) and AAA.

The chemical shifts of the AAM tactic triads are, in ppm:

$mm' = 121.7$; $m'r$ or $r'm = 121.2$ and $r'r = 120.9$

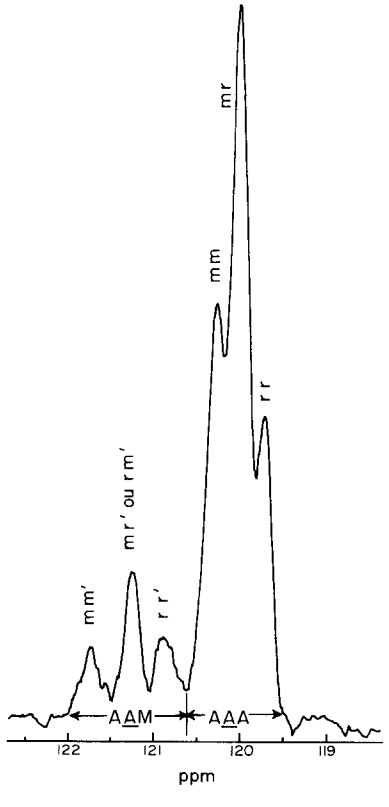

Fig. 12. Expanded ^{13}C spectrum of the CN groups of a copolymer with 8% methacrylic acid units (18,000 transients) and triads attributions.

m' and r' are (MA) diads in which the COOH group is at the same and opposite side of the CN group respectively. For the chemical shifts of the three tactic AAA triads, their values do not differ from those for polyacrylonitrile homopolymers. The experimental ratios of relative intensities are:

$$\frac{(AM)}{(AM)+(AA)}(C\beta \text{ resonances}) = \frac{(AAM)}{(AAM)+(AAA)}(CN \text{ resonances}) \simeq 0.18 \pm 0.01.$$

This value is very close to that computed from the reactivity ratios (0.169). The homo PA sequences of PMA have the same tacticity as the homopolymer (Table 4), whereas the tacticity of MMA triads is: $m'm = 0.25$, $m'r + r'm = 0.50$ and $r'r = 0.25$. The trend of MAA to be more cosyndiotactic should be due to the higher steric hindrance of methacrylic acid units (polymethacrylic acid is more syndiotactic than polyacrylonitrile). Finally it is interesting to note that the stereosequence propagation in the copolymer is Bernouillian as in the homopolymers.

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