Determination of compositional and configurational sequence distribution of acrylonitrile–methyl methacrylate copolymers by ^{13}C n.m.r. spectroscopy

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Acrylonitrile–methyl methacrylate (AM) copolymers of different monomer concentrations were prepared in bulk by free radical initiation. ^{13}C n.m.r. spectra of several acrylonitrile–methyl methacrylate copolymers are discussed in terms of their triad monomer sequence and cotacticity. Terminal and penultimate reactivity ratios were calculated using the observed monomer triad sequence distribution obtained from ^{13}C n.m.r. spectra. Triad sequence distributions were used to calculate diad concentrations, probability parameters, number average sequence lengths and the comonomer mole fractions in the copolymers. The experimental fractions of all the ten A centred and ten M centred triad cotactic sequences were found to be in excellent agreement with those calculated using the probabilities parameters.

(Keywords: acrylonitrile; methyl methacrylate; Harwood program; cotacticities; configurational probabilities)

INTRODUCTION

Acrylonitrile–methyl methacrylate (AM) copolymer is an industrially important copolymer. Detailed evaluation of sequence distribution (triad, tetrad, pentad, etc.) and cotacticity is an effective aid to understand the copolymerization mechanism and to establish the relationships between the sequence distribution and the polymer properties. Guillot *et al.*[1–3] showed that the penultimate model is satisfactory for acrylonitrile– methyl methacrylate copolymerization. Harwood *et al.*[4] reported the proton n.m.r. of acrylonitrile–methyl methacrylate copolymers prepared in THF and DMF. Their results were consistent with those reported by Guillot *et al.*

Ritchey *et al.*[5] reported the ^{13}C n.m.r. of series of acrylonitrile–methyl methacrylate copolymers and determined the copolymer microstructure. They reported the configuration probabilities of acrylonitrile–methyl methacrylate copolymers and Bernoullian statistics were found to describe the monomer configuration, a result in conflict with the conclusions of Pham[6]. Ritchey *et al.*[5] assigned the resonance lines of carbonyl and nitrile carbons to different triad cotactic sequences on the assumption that M and A monomer units have the same sensitivity to the tacticity of an adjacent A monomer unit. Also they did not calculate cotactic triad fractions from ^{13}C n.m.r. spectra and no comparison of experimental cotactic triad fractions with those expected from configurational probabilities have been made.

In this manuscript we report the ^{13}C n.m.r. spectra of a series of acrylonitrile–methyl methacrylate copolymers. The primary structure, including monomer composition, monomer sequence distribution and triad tacticity of AM copolymers have been determined on the basis of $^{13}C\{^1H\}$ n.m.r. analysis and compared with the calculated fractions. The resonance of carbonyl and nitrile carbons have been assigned to different cotactic triads by considering the possible electronic interactions between the central monomer unit and its immediate neighbours.

EXPERIMENTAL

Acrylonitrile and methyl methacrylate monomers were vacuum distilled and stored at temperatures below 5°C. A monomer mixture was taken in a round bottom flask and 0.5% of benzoyl peroxide was added. Purified nitrogen was flushed in and the polymerization was allowed to proceed at 70°C. The percentage conversion was kept below 5% by precipitating the copolymers in excess of methanol after 30 min. A series of copolymers having different comonomer concentration were prepared by a similar method.

^1H and $^{13}C\{^1H\}$ n.m.r. spectra of all samples were recorded with a Jeol FX 100 n.m.r. spectrometer, operating at 99.5 and 25 MHz, respectively, in DMSO-d_6 at 120°C. The other conditions of recording and details of curve fitting have been described elsewhere[7–10].

The molecular weights of the copolymer samples were determined on a Waters g.p.c. instrument at 25°C using a 5μ-PL-gel mixed column. THF was the mobile phase and a refractive index detector was used. Calibration was done with PMMA reference standards. Elemental analyses were done on a Perkin Elmer 240C elemental analyser.

RESULTS AND DISCUSSION

Composition of the AM copolymers was estimated by the percentage nitrogen content of the copolymers. *Table 1* shows the comonomer mole fractions in feed and in

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Table 1 Copolymer composition data and molecular weight distribution for acrylonitrile (A)–methyl methacrylate (M) copolymers prepared at 70°C. f is the mole fractions of monomers in feed; F is the mole fractions of monomers in copolymer; M_n is the PMMA equivalent number average molecular weight; M_w is the PMMA equivalent weight average molecular weight and M_w/M_n is the polydispersity

f_A	f_M	% Nitrogen	F_A	F_M	$M_n \times 10^{-5}$	$M_w \times 10^{-5}$	M_w/M_n
0.790	0.210	11.14	0.579	0.421	1.28	1.62	1.28
0.700	0.300	8.90	0.489	0.511	1.88	2.37	1.26
0.595	0.405	6.96	0.403	0.597	1.69	2.33	1.38
0.483	0.517	4.58	0.283	0.717	2.05	2.76	1.34
0.396	0.604	4.29	0.268	0.732	2.37	3.01	1.27
0.282	0.718	3.13	0.202	0.798	2.22	3.01	1.35

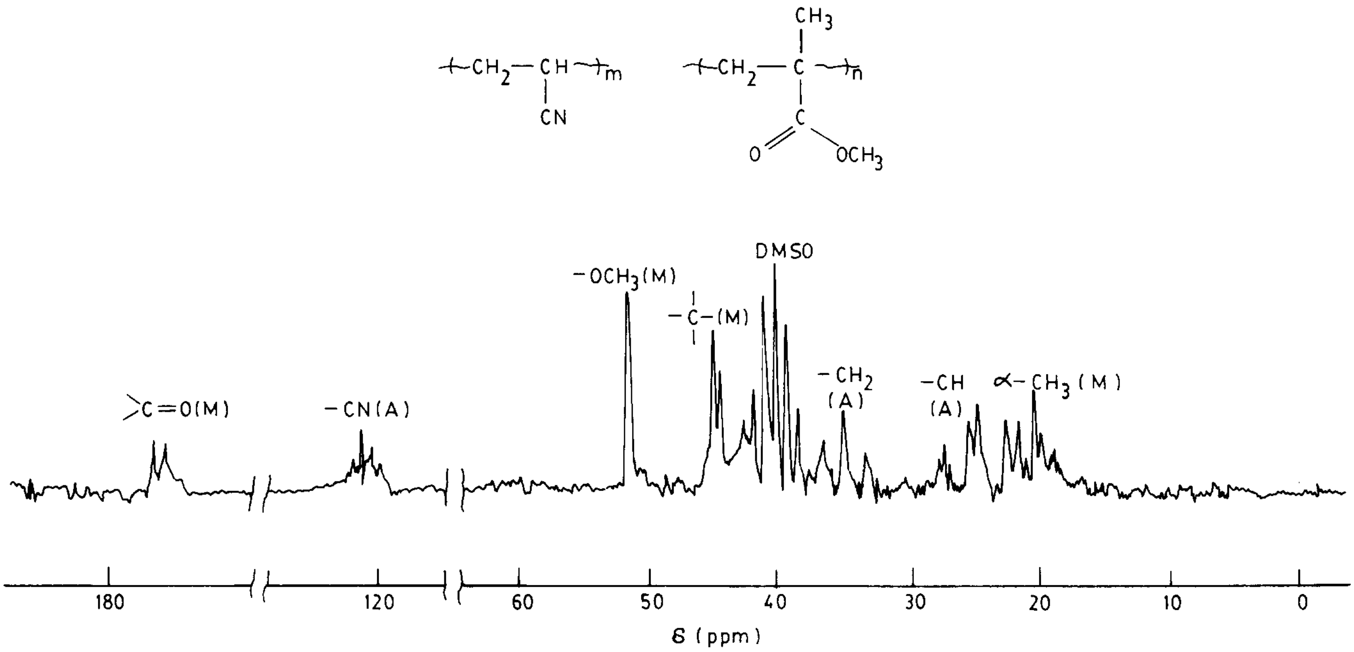


Figure 1 25 MHz $^{13}C\{^1H\}$ n.m.r. spectrum of acrylonitrile (A)–methyl methacrylate (M) copolymer (79.0 mol% of A in feed) recorded in DMSO-d_6 solution at 120°C

the copolymers along with the percentage nitrogen in the copolymers. Copolymer composition data were used to calculate the terminal model reactivity ratios by the method of Kelen and Tudös[15]. The values of reactivity ratios obtained from the Kelen–Tudos plot are $r_A = 0.21 \pm 0.04$ and $r_M = 1.42 \pm 0.032$. The reactivity ratio values are in good agreement with those reported in the literature[4,5].

The PMMA equivalent number average (M_n), weight average (M_w) molecular weight and the polydispersity of AM copolymer samples are given in *Table 1*. The M_w varies from 1.6×10^5 to 3.0×10^5 and M_n varies from 1.2×10^5 to 2.5×10^5. The polydispersity value for the samples is almost the same for all the copolymer samples (≈ 1.3). The heterogeneity of the copolymer samples is almost of the same order and the molecular weight distribution is of the same nature.

A 25 MHz $^{13}C\{^1H\}$ n.m.r. spectrum of the AM copolymer (A = 79.0 mol% in feed), recorded in DMSO-d_6 at 120°C is shown in *Figure 1*. The various resonance peaks have been assigned previously[5] and are shown in *Figure 1*. The carbonyl (>C=O) carbon expansions of AM copolymers are shown in *Figure 2*. The three sets of lines whose intensities change with copolymer composition can be assigned to carbonyl centred in MMM, MMA(AMM) and AMA triad sequences from low to high field. The tacticities of the MMM sequence have already been identified[11]. The other resonances and shoulders comprising AMM and AMA sequences can be attributed to the four AMM(MMA) cotacticities. Concentrations of various M centred triads can be calculated from the relative area of the resonance peaks. Similar compositional information regarding the A-centred triads can be made using the nitrile (–CN) carbon resonance region. *Figure 3* shows the expanded nitrile resonance for the series of AM copolymers. Resonance peaks due to the AAA triad are expected to appear most upfield and that of the MAM triad to be most downfield. Recently, Kamide *et al.*[13] evaluated the pentad tacticity of PAN using the –CN carbon peak. *Table 2* contains the compositional information concerning the various M-centred and A-centred triads along with the distribution obtained by Harwood's program[12] using the terminal model reactivity ratios ($r_A = 0.21$ and $r_M = 1.42$).

Penultimate reactivity ratios (r_{MM}, r_{AM}, r_{AA} and r_{MA}) were evaluated from the experimentally obtained triad distributions and the average monomer feed ratios[4]. The values of penultimate reactivity ratios are listed for individual samples in *Table 2*. The reactivity ratios are in good agreement with values determined by Harwood *et al.*[4]. Using the average values of penultimate reactivity ratios, the triad sequence distributions were obtained by

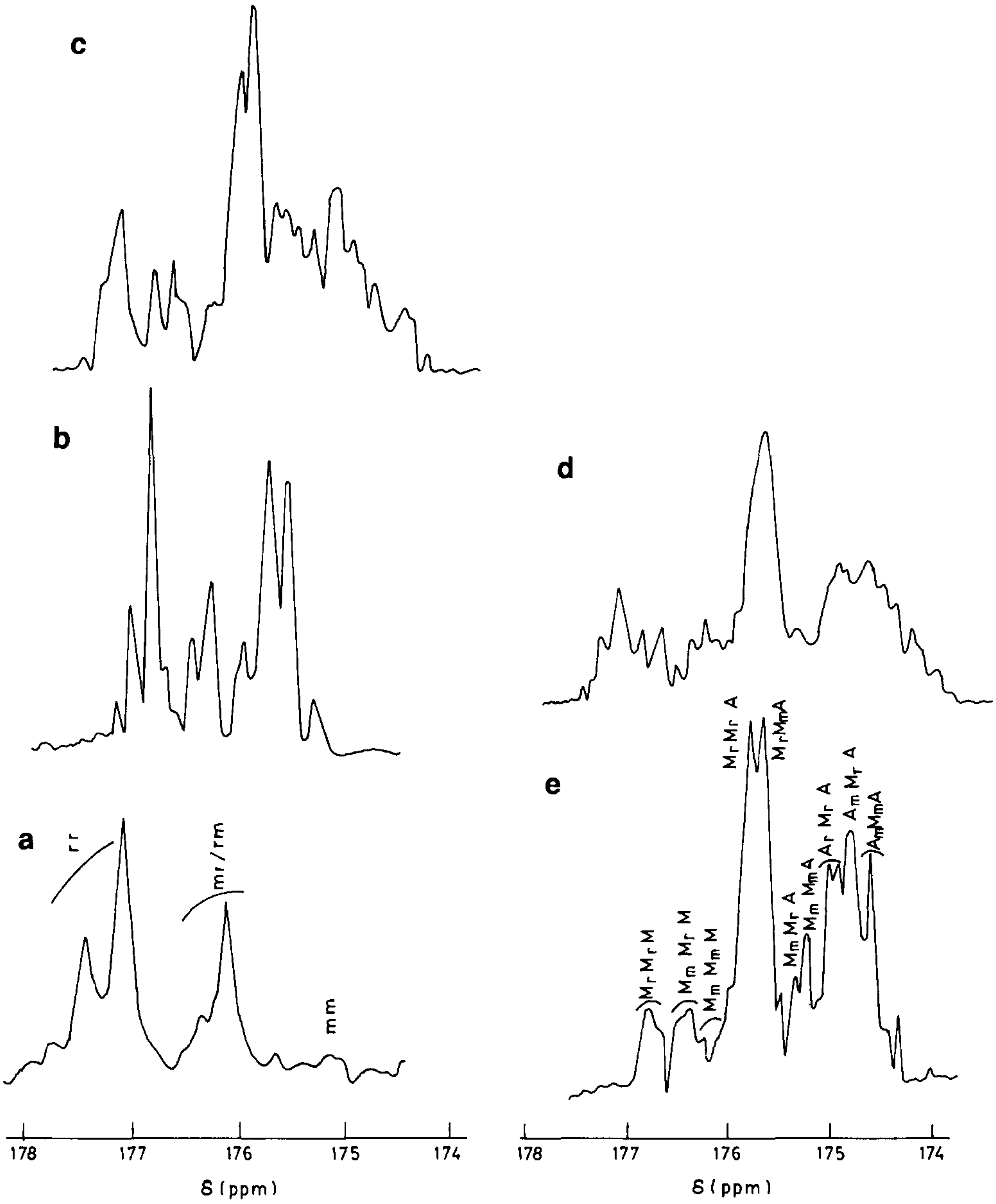


Figure 2 Expanded carbonyl (>C=O) carbon resonance spectra for acrylonitrile (A)–methyl methacrylate (M) copolymer; mol% of M in feed is (a) 100%; (b) 60.4%; (c) 40.5%; (d) 30.0%; (e) 21.0%

Harwood's program and given in *Table 2*. It is not possible to discriminate between two models on the basis of this data.

From the results of composition with respect to various A and M centred triads, the conditional P_{AM} and P_{MA} has been calculated using the following equations:

$$P_{AM} = \frac{[MAM] + [MAA]/2}{[MAM] + [MAA] + [AAA]} \quad (1a)$$

$$P_{MA} = \frac{[AMA] + [MMA]/2}{[AMA] + [MMA] + [MMM]} \quad (1b)$$

where P_{AM} is the probability that an A–M unit comes about as a result of an A-growing chain end adding M and P_{MA} is the probability that an M–A unit comes about as a result of M-growing chain end adding A. Parameters in square brackets are the fractions of various triads, determined by ^{13}C n.m.r. spectroscopy. The number average sequence lengths ($\bar{N}_A$ and $\bar{N}_M$) are the reciprocal of the conditional probabilities and can also be obtained. *Table 3* contains the copolymerization parameters of AM copolymers for different monomer feed concentrations.

These triad compositional distributions from ^{13}C n.m.r. have been used to calculate the monomer compositions of copolymers. The compositions of three possible diads, i.e. AA, AM and MM can be calculated from the resonance of carbonyl and nitrile carbons as follows:

$$[AA] = [AAA] + [MAA]/2 \quad (2a)$$

$$[MM] = [MMM] + [AMM]/2 \quad (2b)$$

Thus the composition of the A–M diad can be readily calculated:

$$[AM] = 1 - [AA] - [MM] \quad (2c)$$

Monomer composition of acrylonitrile (A) and methyl methacrylate (M) are easily calculated from the diad compositions in a similar way:

$$[A] = [AA] + [AM]/2 \quad (3a)$$

$$[M] = [MM] + [AM]/2 \quad (3b)$$

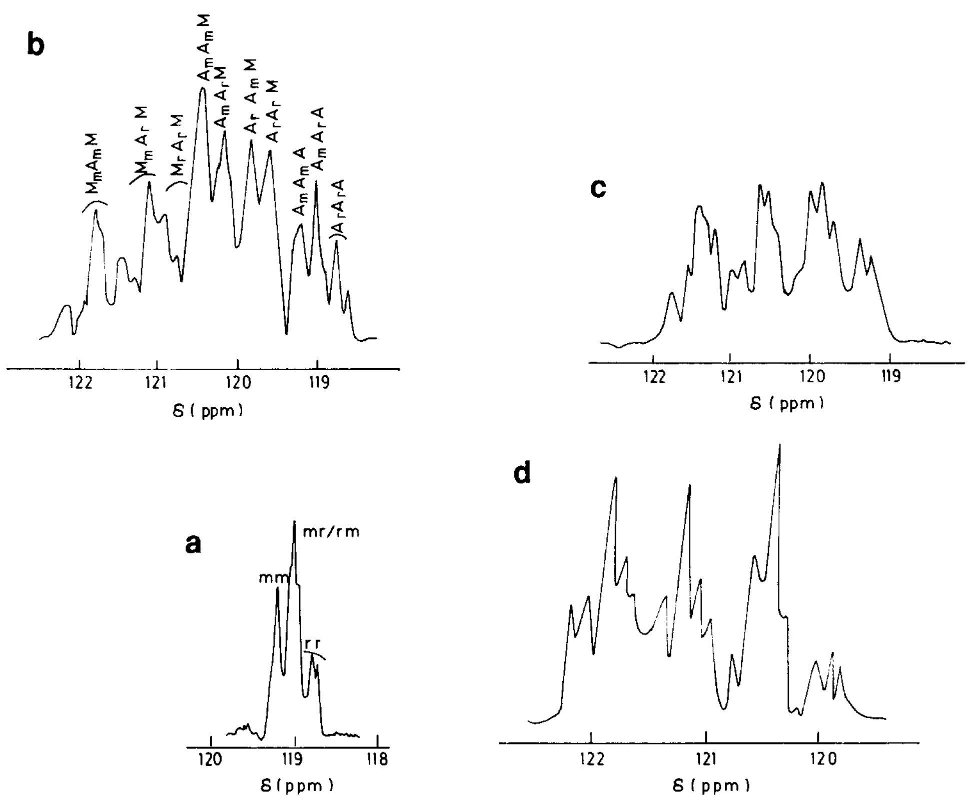


Figure 3 Expanded nitrile (-CN) carbon resonance spectra for acrylonitrile (A)-methyl methacrylate (M) copolymer; mol% of A in feed is (a) 100%; (b) 79.0%; (c) 59.5%; (d) 39.6%

Table 2 Calculated and observed fractions of A and M centred triads in acrylonitrile (A)-methyl methacrylate (M) copolymers

A mol%	Triad	Fraction Obs[a]	Ter[b]	Pen[c]	Penultimate reactivity ratios
	AAA	0.281	0.195	0.278	$r_{AA} = 0.326$, $r_{MA} = 0.187$
	AAM	0.431	0.493	0.441	
79.0	MAM	0.288	0.312	0.281	$r_{MM} = 1.17$, $r_{AM} = 1.53$
	MMM	0.060	0.075	0.057	
	MMA	0.410	0.398	0.417	
	AMA	0.530	0.527	0.525	
	AAA	0.065	0.056	0.081	$r_{AA} = 0.33$, $r_{MA} = 0.22$
	AAM	0.346	0.360	0.340	
59.5	MAM	0.589	0.584	0.579	$r_{MM} = 1.13$, $r_{AM} = 1.49$
	MMM	0.201	0.242	0.199	
	MMA	0.531	0.500	0.544	
	AMA	0.268	0.258	0.257	
	AAA	0.023	0.015	0.021	$r_{AA} = 0.324$, $r_{MA} = 0.209$
	AAM	0.213	0.213	0.203	
39.6	MAM	0.764	0.772	0.776	$r_{MM} = 0.99$, $r_{AM} = 1.72$
	MMM	0.384	0.468	0.405	
	MMA	0.516	0.432	0.492	
	AMA	0.100	0.100	0.103	

[a] By ^{13}C n.m.r. spectroscopy using the carbonyl carbon and nitrile carbon resonance for M and A centred triad fractions respectively
[b] By terminal model Harwood's program
[c] By penultimate model Harwood's program

Table 4 gives the diad and monomer concentrations calculated from the observed triad distribution as determined from ^{13}C n.m.r. spectroscopy. The monomer compositions obtained are in good agreement with those calculated by the nitrogen analyses.

Cotacticities of AM copolymers

The tacticity of free radical polymerized homopolymers obeying Bernoullian statistics can be described in terms of two probabilities: P_m, the probability of adding meso, and P_r, the probability of adding racemic, where

Table 3 Copolymerization parameters in acrylonitrile (A)–methyl methacrylate (M) copolymers determined by ^{13}C n.m.r. spectroscopy. P_{AM} is the probability that A–M unit comes about as a result of A-growing chain end adding M. P_{MA} is the probability that M–A unit comes about as a result of M-growing chain end adding A. $\bar{N}_A$ is the number average sequence length of acrylonitrile and $\bar{N}_M$ is the number average sequence length of methyl methacrylate

A (mol%)	P_{AM}	P_{MA}	$\bar{N}_A$	$\bar{N}_M$
79.0	0.504	0.735	1.98	1.36
59.5	0.730	0.534	1.37	1.87
39.6	0.870	0.358	1.15	2.79

Table 4 Copolymer composition and diad fractions determined by observed triad fractions

A (mol%)	Diad fraction	[A]	[M]
79.0	[AA] = 0.496 [MM] = 0.265 [AM] = 0.239	0.616 (0.579)[a]	0.384 (0.421)
59.5	[AA] = 0.270 [MM] = 0.469 [AM] = 0.261	0.401 (0.403)	0.599 (0.597)
39.6	[AA] = 0.130 [MM] = 0.638 [AM] = 0.232	0.244 (0.268)	0.756 (0.732)

[a] Values in parenthesis are the comonomer composition obtained by nitrogen analyses

$P_m + P_r = 1$. The same type of probabilities can be used to describe the cotacticities in copolymers, where along with P_m and P_r, two additional probabilities must be defined. These are P'_m and P'_r, where P'_m is the probability of meso addition of two dissimilar monomers and P'_r is the probability for racemic addition of two dissimilar monomers, e.g. the four cotacticities for the triad sequences AAM and MMA have been labelled as mm′, rm′, mr′ and rr′. The expression giving the concentrations of various M centred cotactic triad sequences can be given as:

$$[\mathrm{MmMmM}] = F_{\mathrm{MMM}} P_m \times P_m \tag{4a}$$

$$[\mathrm{MmMrM}] = 2 \times F_{\mathrm{MMM}} P_m \times P_r \tag{4b}$$

$$[\mathrm{MrMrM}] = F_{\mathrm{MMM}} P_r \times P_r \tag{4c}$$

$$[\mathrm{AmMmA}] = F_{\mathrm{AMA}} P'_m \times P'_m \tag{4d}$$

$$[\mathrm{AmMrA}] = 2 \times F_{\mathrm{AMA}} P'_m \times P'_r \tag{4e}$$

$$[\mathrm{ArMrA}] = F_{\mathrm{AMA}} P'_r \times P'_r \tag{4f}$$

$$[\mathrm{MrMrA}] = F_{\mathrm{MMA}} P_r \times P'_r \tag{4g}$$

$$[\mathrm{MmMmA}] = F_{\mathrm{MMA}} P_m \times P'_m \tag{4h}$$

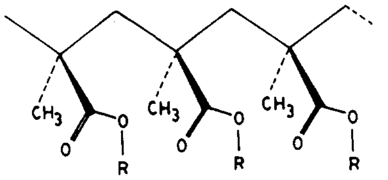
$$[\mathrm{MmMrA}] = F_{\mathrm{MMA}} P_m \times P'_r \tag{4i}$$

$$[\mathrm{MrMmA}] = F_{\mathrm{MMA}} P_r \times P'_m \tag{4j}$$

where F_{MMM}, F_{MMA} and F_{AMA} are the fractions of the respective triads. Similar expressions can be written for A centred cotactic triad sequences.

Assignment and determination of nitrile and carbonyl carbon cotacticities

The ^{13}C n.m.r. spectra and the triad tacticities of the carbonyl (–CO) and the nitrile (–CN) carbons of polymethyl methacrylate (PMMA) and polyacrylonitrile (PAN) are shown in *Figures 2a* and *3a* respectively. Free radical polymerized PMMA is primarily syndiotactic with Pr being 0.79. The most upfield peaks at ≈δ 175.68 ppm in the –CO carbon resonance have been assigned to isotactic (mm) triad[11]. The preferred conformation of the isotactic alkyl methacrylate chain[14] is:



where R = $-CH_3$, $-C_2H_5$ etc., and in this case interactions between the oxygen of the –CO group and hydrogen of the alkyl group can take place. The initial deshielding effect on the –CO carbon is decreased because of these interactions and by the diamagnetic shielding effects from the anisotropy of the immediate –CO neighbours. This kind of interaction cannot take place in syndiotactic (rr) triad and rr triad appears down field at ≈δ 177.77 ppm. PAN prepared by free radical polymerization is atactic in nature. The most down field peak has been assigned to mm triad because of the interactions of the central –CN with the adjacent –CN groups to form a six membered ring in this case[13]. The resultant double bond nature of the –CN group leads to diminishing of the electron density on a –CN carbon, and the disappearing of the shielding effect originally existing on the –CN carbon is a racemic (r) arrangement.

While making the peak assignments in the case of different cotactic sequences for the MMA, AMA, AAM and MAM monomer triads, Ritchey *et al.*[5] assumed that the central nitrile and carbonyl carbons in the AAM, MAM, MMA and AMA triad sequences are affected by the tacticity of the neighbouring monomers in the same manner as the tacticity of the neighbouring monomers affect the central nitrile and carbonyl carbons in the homopolymers. But an M monomer unit and an A monomer unit will not have the same sensitivity to the tacticity of an adjacent A monomer because of the various electronic interactions between the central monomer unit and its immediate neighbours in different triad sequences. These interactions may lead to a shielding or deshielding effect on the carbon of the central unit depending on the configurations of the adjacent M and A unit.

In the case of MMA triad, the central –CO carbon will have a diamagnetic shielding effect from a M unit in m configuration as in PMMA. Similarly an A unit attached to a central M unit in m configuration will result in the interaction between the hydrogen of $-OCH_3$ protons and nitrogen of the –CN group. This interaction again leads to the increased electron density on the central –CO carbon and decreased electron density on the –CN carbon because of the decreased triple bond character. This kind of interaction is not possible in an MrMrA cotactic triad sequence and hence there is no induced diamagnetic shielding effect. This cotactic triad is expected to appear most downfield out of the four possible cotactic sequences. Out of MmMrA and MrMmA sequences, the central –CO will have interaction with M and A units in the respective sequences. The electron inbooting effect in case of MmM– is more as compared to the –MmA sequence and is supported by the chemical shift values for different tactic triad sequences in homopolymers. The MmMrA triad will appear upfield as compared to the MrMmA triad. Thus the lines corresponding to MMA sequences are assigned to cotacticities as rr′ (δ 176.04 ppm), rm′ (δ 175.82 ppm), mr′ (δ 175.50 ppm) and mm′ (δ 175.32 ppm) from low to high field, respectively. Considering similar kinds of interactions and their relative effects, the lines of the -CO carbon resonance for the AMA sequence are assigned as r′r′ (δ 175.10 ppm), r′m′/m′r′ (δ 174.80 ppm), and m′m′ (δ 174.45 ppm). Small shoulders on the main peaks are due to the higher ad effects of the various comonomer and stereochemical sequences (*Figure 2b*).

As in the case of the AAM triad, in the AmAmM cotactic sequence, the central -CN group can have interactions with both the monomer units and forms a six membered ring system. The double bond nature introduced in the central -CN group leads to a downfield shift. For an ArArM sequence, because of the absence of these kinds of interactions, the original diamagnetic effect on the central -CN group will result in the upfield shift. Our of AmArM and ArAmM, the AmArM sequence is expected to appear downfield because a -CN group can have better interaction with a -CN group as compared with $-OCH_3$ group. Therefore, the four cotacticities for the nitrile in the AAM sequence can be assigned from low to high field as mm′ (δ 120.65 ppm), mr′ (δ 120.45 ppm), rm′ (δ 119.96 ppm), and rr′ (δ 119.63 ppm). Similarly, the most downfield lines of the MAM sequence may be the coisotactic sequence (m′m′) at $\approx\delta$ 122.05 ppm followed by coheterotactic sequence (m′r′) at $\approx\delta$ 121.65 ppm. Most upfield lines are due to cosyndiotactic sequence (r′r′) at $\approx\delta$ 121.00 ppm (*Figure 3b*).

Probabilities like P_m and P_r for PMMA and PAN homopolymers have been determined from the quaternary carbon and the nitrile carbon resonances, respectively. The values obtained were $P_m = 0.52$, $P_r = 0.48$ for PAN and $P_m = 0.21$ and $P_r = 0.79$ for PMMA. The same procedure was adopted for calculating P'_m and P'_r, i.e. by determining the areas of the lines corresponding to different cotactic triad sequences. For example, the areas of the four cotactic lines of the AAM nitrile carbon may be related using the same notation as the previous discussion of cotacticity:

$$\mathrm{mr}' = P_m P'_r$$

$$\mathrm{rr}' = P_r P'_r$$

$$\mathrm{mm}' = P_m P'_m$$

$$\mathrm{rm}' = P_r P'_m$$

where $\mathrm{mr}' + \mathrm{rr}' + \mathrm{mm}' + \mathrm{rm}' = 1$.

From the area of these lines the individual probabilities like P_m, P_r, P'_m and P'_r have been obtained. The configurational probabilities of AM copolymers obtained from the ^{13}C n.m.r. of the carbonyl and nitrile carbons are given in *Table 5*. These values were then substituted in the expressions like (4a–j) for the calculation of all the twenty cotactic triad monomer sequences concentration.

The populations of all the twenty tactic monomer sequence triads in the AM copolymer samples calculated using the probability parameters and those obtained from ^{13}C n.m.r. spectra are given in *Table 6*. The observed and the calculated tactic triad sequence populations are in fairly good agreement. The -MM- sequence in an MMM and MMA triad has a slightly different value of P_r. Similarly, the -AA sequence in the AAA and AAM triad has a different value of P_r. The cotacticity of -MA- sequence is random as evident from the values of P'_m and P'_r. The results in *Table 5* show that the Bernoullian statistics can satisfactorily describe the monomer configuration in acrylonitrile–methyl methacrylate copolymers. The tacticities of -MM- and the -AA- diads in the copolymer are identical to tacticities in homopolymers. The cotacticity of the -AM- diad is also random and indicates that the M and A monomer unit do not interact sterically during the copolymerization.

Table 5 Configurational probabilities of acrylonitrile–methyl methacrylate (AM) copolymers from the ^{13}C n.m.r. of the carbonyl and nitrile carbons

Mol% of A (in feed)	
79.0	59.6
MMM sequence	MMM sequence
Pr = 0.79	Pr = 0.79
Pm = 0.21	Pm = 0.21
AAA sequence	AAA sequence
Pr = 0.48	Pr = 0.48
Pm = 0.52	Pm = 0.52
MMA sequence	MMA sequence
Pr = 0.738	Pr = 0.733
Pm = 0.262	Pm = 0.267
Pm′ = 0.480	Pm′ = 0.545
Pr′ = 0.520	Pr′ = 0.445
AAM sequence	AAM sequence
Pr = 0.480	Pr = 0.480
Pm = 0.520	Pm = 0.520
Pm′ = 0.480	Pm′ = 0.545
Pr′ = 0.520	Pr′ = 0.445

Table 6 Evaluation of the ten monomer sequence distribution cotactic triads for A-centred and M-centred groups

	79.0% A		59.6% A	
	Cal[a]	Obs[b]	Cal	Obs
[MrMrM]	0.048	–	0.125	0.128
[MmMrM]	0.025	–	0.067	0.064
[MmMmM]	0.003	–	0.009	0.010
[MrMrA]	0.157	0.149	0.173	0.168
[MrMmA]	0.145	0.161	0.212	0.221
[MmMrA]	0.056	0.057	0.063	0.090
[MmMmA]	0.052	0.043	0.077	0.052
[ArMrA]	0.122	0.117	0.053	0.045
[AmMrA]	0.265	0.250	0.137	0.134
[AmMmA]	0.143	0.156	0.078	0.089
[MmAmM]	0.078	0.080	0.175	0.196
[MmArM]	0.144	0.140	0.292	0.282
[MrArM]	0.066	0.065	0.122	0.111
[AmAmM]	0.108	0.109	0.098	0.096
[AmArM]	0.116	0.091	0.081	0.075
[ArAmM]	0.099	0.124	0.091	0.099
[ArArM]	0.108	0.107	0.074	0.074
[AmAmA]	0.065	0.054	0.018	–
[AmArA]	0.140	0.126	0.032	–
[ArArA]	0.076	0.100	0.040	–

[a] Calculated fractions using the configurational probabilities
[b] Observed fractions from the ^{13}C n.m.r. spectra

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