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2D NMR studies of acrylonitrile–methyl acrylate copolymers

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Abstract

The microstructure of acrylonitrile–methyl acrylate copolymers prepared by the solution polymerization using 2,2′-azobisisobutyronitrile (AIBN) as free radical initiator was investigated by two-dimensional NMR techniques. 2D-heteronuclear single quantum correlation (HSQC) and the total correlation spectroscopy (TOCSY) have been utilized to resolve the complex ^{1}H NMR spectrum and to establish the compositional and configurational sequences of acrylonitrile–methyl acrylate copolymers. 2D HSQC and TOCSY showed compositional and configurational sensitivity of methine protons of A and M units upto the triad level. Heteronuclear multiple-bond correlation (HMBC) spectroscopy has been used to study carbon (carbonyl/nitrile)–proton coupling. The carbonyl and nitrile carbons showed compositional sensitivity upto the triad level. The values of reactivity ratios were determined by Kelen–Tudos (KT) and non-linear error in variable method (RREVM).

Keywords: Solution copolymerization; Acrylonitrile–methyl acrylate copolymer; NMR

1. Introduction

Acrylonitrile copolymers are of tremendous interest in many industrial applications e.g. as adhesives and binders, surface coatings, antioxidants, viscosity index improvers, emulsifying agents, insecticides, plasticizers, asphalt additives, artificial organ material, crosslinking agents, etc. [1]. Such a wide range of applications can be attributed to the appropriate choice of the pendent group in the copolymer system.

The microstructure of the copolymers is stereochemical as well as compositional arrangements of various monomer units and it is the factor which is responsible for the physical and chemical properties of the copolymer and thus very useful in tailoring copolymers with desired properties.

NMR spectroscopy has been used as a powerful experimental technique to determine the intramolecular and intermolecular chain structures of vinyl copolymers [2–11]. One of the main established functions of NMR in polymer science is the structural characterization of the copolymers, which provides the link between structure–property relationships [12–14].

Two-dimensional NMR spectroscopy tenders a powerful tool for the stereochemical investigation of polymers. 2D heteronuclear NMR spectroscopy is being

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used for the study of homopolymers as well as copolymers [15–23]. 2D TOCSY experiment is used to study the spin relay coupling through the magnetization transfer in the copolymers. The heteronuclear correlation experiments like HSQC and HMBC use the inverse spectroscopy in the proton detection and thus improve the sensitivity of the $^{13}C\{^1H\}$ spectrum. On the basis of the covalent interactions, these methods together make all carbons in the molecule detectable at natural abundance and thus deliver structural information along chemical bond network of the molecule.

Matsuzaki et al. [24] have reported the $^{13}C\{^1H\}$ NMR spectra of poly(acrylates) as well as their model compounds and also the stereo regularity of poly(methylacrylate) [25]. Recently, Wiles et al. [6] have determined monomer reactivity ratios for acrylonitrile and methyl acrylate copolymer system from ^1H NMR and real time Fourier transform infrared spectroscopy. Our group, in earlier publications has reported microstructure of acrylonitrile, alkyl acrylate, alkyl methacrylate, etc. copolymers using 1D NMR spectroscopy [26–34]. In the present investigations, $^{13}C\{^1H\}$ NMR, HSQC, TOCSY and HMBC techniques have been used to determine the composition and configurational sequences of acrylonitrile and methyl acrylate copolymer.

2. Experimental

Acrylonitrile and methyl acrylate (A and M) monomers were distilled under reduced pressure and stored below 5 °C. A series of acrylonitrile/methyl acrylate (A/M units) copolymers containing different mole fractions of acrylonitrile in feed, were prepared by solution polymerization using DMF (*N*,*N*-dimethylformamide) as solvent and AIBN as an initiator at 60 °C. The conversion was kept below 10% by precipitating the copolymers in methanol, redissolved in DMSO/chloroform and then reprecipitated again in excess of methanol.

2.1. NMR experiment

^1H and $^{13}C\{^1H\}$ NMR experiments were performed in $CDCl_3$ and DMSO-d_6 (for PAN and $F_A = 0.70$) on Bruker 300 MHz DPX spectrometer at frequency of 300.13 MHz and 75.5 MHz, respectively. The quantitative $^{13}C\{^1H\}$ NMR experiments were carried out using the inverse-gated decoupling pulse program with 12 s as a delay time ($5t_1$). All two-dimensional experiments were carried out on 300 MHz DPX spectrometer having a dual probe. The pulse sequence invigpt and invgplrnd of the bruker software were used to record gradient

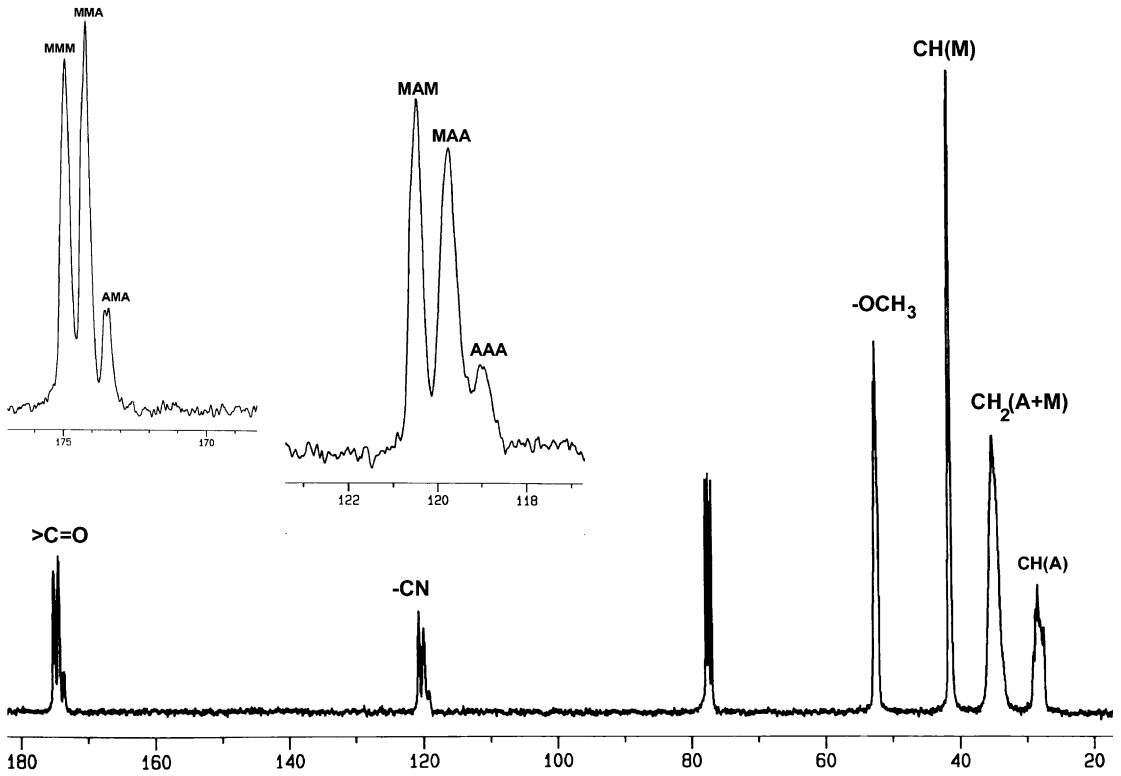


Fig. 1. $^{13}C\{^1H\}$ NMR spectrum of A/M copolymer ($F_A = 0.36$) in $CDCl_3$ also displaying expanded nitrile and carbonyl regions.

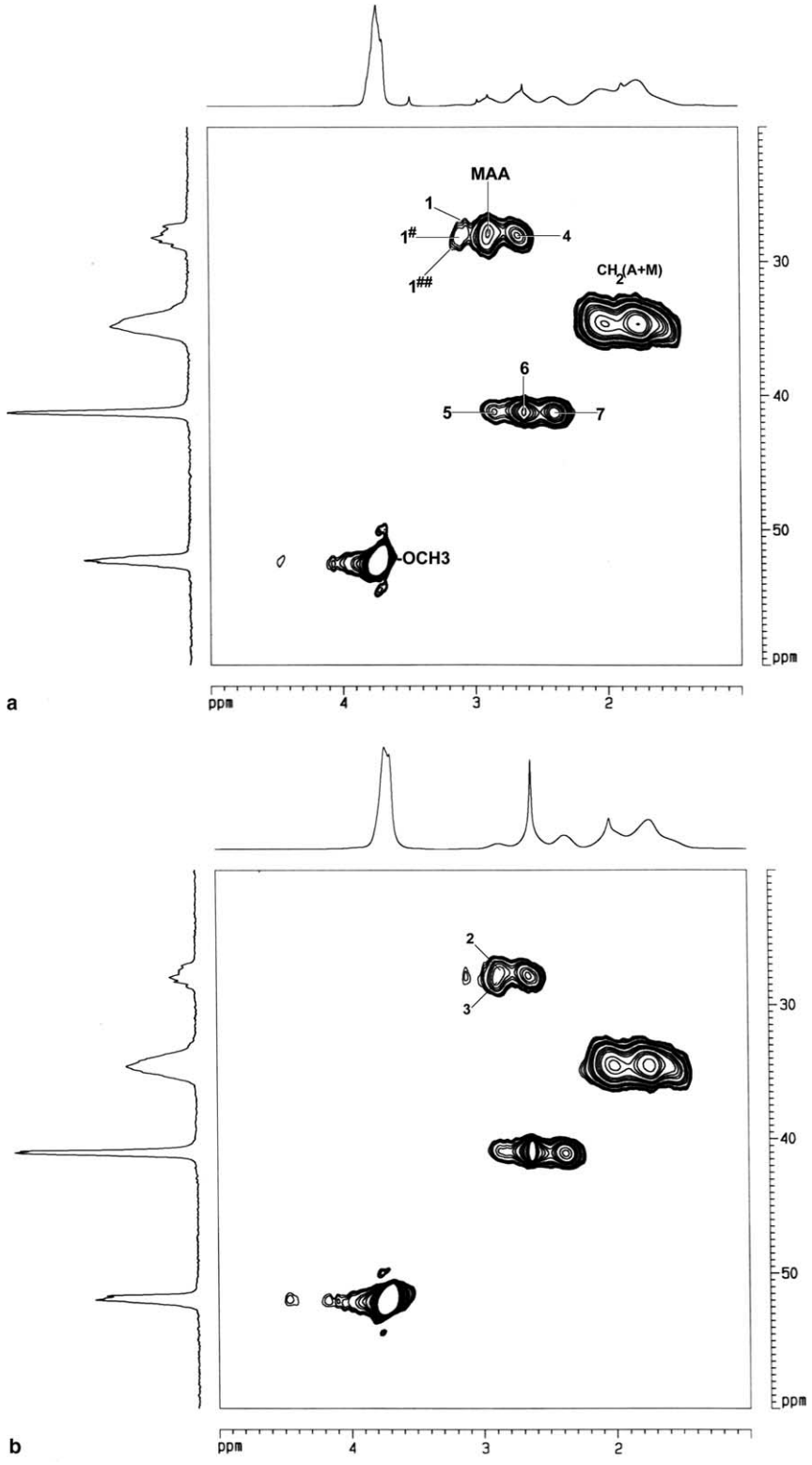


Fig. 2. 2D HSQC NMR spectra of acrylonitrile/methyl acrylate copolymer showing methine and methylene regions in $CDCl_3$, (a) $F_A = 0.36$, (b) $F_A = 0.26$.

HSQC and HMBC experiments, respectively. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 t_1 experiments. The TOCSY experiment, with 32 scans being collected for each t_1 value, was carried out using standard pulse sequence. A total of 512 spectra each containing the 1 K data points were accumulated [35]. Measurements were made on 5% (w/v) polymer solution.

3. Results and discussion

The composition of A/M copolymers was determined using quantitative $^{13}C\{^1H\}$ NMR. (The relaxation time of carbonyl and nitrile functional groups was observed to be less than 2 s.) The mole fractions of acrylonitrile in feed and in copolymer were 0.70, 0.50, 0.40, 0.30 and 0.74, 0.53, 0.42, 0.34 respectively. The values of reactivity ratios were obtained using copolymer composition data by Kelen–Tudos (KT) [36] r_A=1.21 ± 0.11, $r_M = 0.90 \pm 0.08$ and non-linear error in variable method (RREVM) [37] $r_A = 1.11$, $r_M = 0.84$, indicating that there is random placement of two monomers along the copolymer chain. The reactivity ratios were used to determine the behavior of two monomers in the copolymerization reaction. The reactivity ratio of acrylonitrile monomer was higher ($r_A = 1.11$) than that of methyl acrylate ($r_M = 0.84$), which indicates that the copolymer will contain more of acrylonitrile than methyl acrylate.

3.1. $^{13}C\{^1H\}$ NMR studies

$^{13}C\{^1H\}$ NMR spectra have much larger chemical shift range than ^1H spectra as a result they provide more information. The completely assigned $^{13}C\{^1H\}$ NMR spectrum of acrylonitrile–methyl acrylate copolymer ($F_A = 0.36$) in $CDCl_3$ is shown in Fig. 1. The spectral region δ 118.75–120.84 ppm was assigned to nitrile carbon and δ 173.03–175.29 ppm region was assigned to the carbonyl carbon. Both of these signals show multiplet indicating that they were sensitive toward compositional sequences and can be used for the assessment of the copolymerization mechanism. In the expanded region (Fig. 1) resonance signals δ 118.75–119.25, 119.25–120.17, 120.17–120.84 ppm were assigned to AAA, MAA, MAM triads of the nitrile region and in the carbonyl region (Fig. 1) δ 173.03–173.72, 173.72–174.51, 174.51–175.29 ppm were assigned to AMA, MMA, MMM on the basis of change in the intensity of the signals with the copolymer composition.

3.2. HSQC NMR studies

Correlation between carbon and proton signals were obtained from the ^1H–^{13}C heteronuclear single quantum

Table 1
Spectral assignments of methine region of acrylonitrile/methyl acrylate based on HSQC spectra

Peak no.	Assignments	HSQC	
		^{13}C (ppm)	^1H (ppm)
1	AmAmA	27.57	3.06
1#	AmArA	28.13	3.13
1##	ArArA	28.67	3.10
2	AmAM	28.00	2.89
3	ArAM	27.39	2.86
4	MAM	27.92	2.67
5	AMA	41.15	2.85
6	AMM	41.42	2.63
7	MMM	41.28	2.39

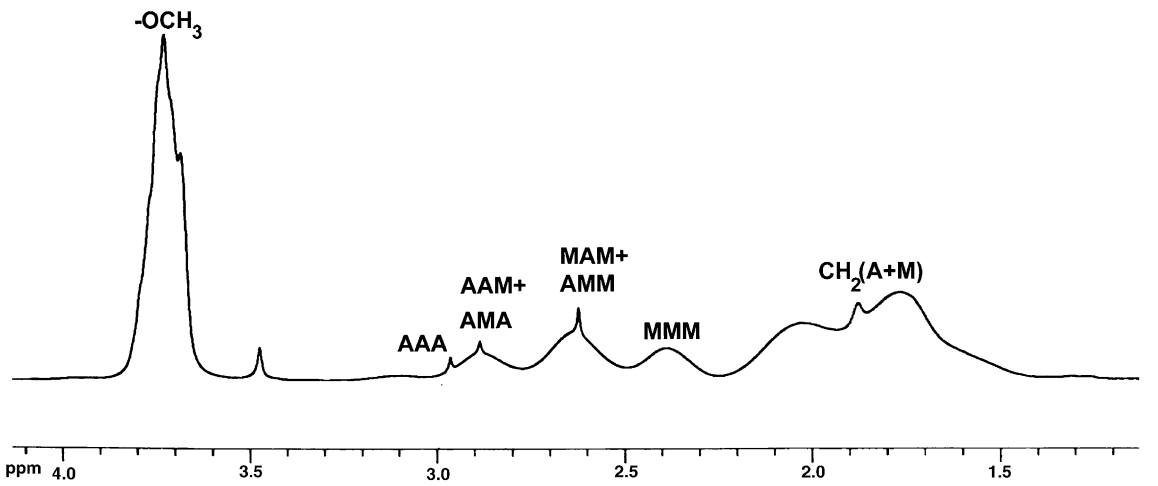


Fig. 3. ^1H NMR spectrum of acrylonitrile/methyl acrylate copolymer for $F_M = 0.36$ in $CDCl_3$.

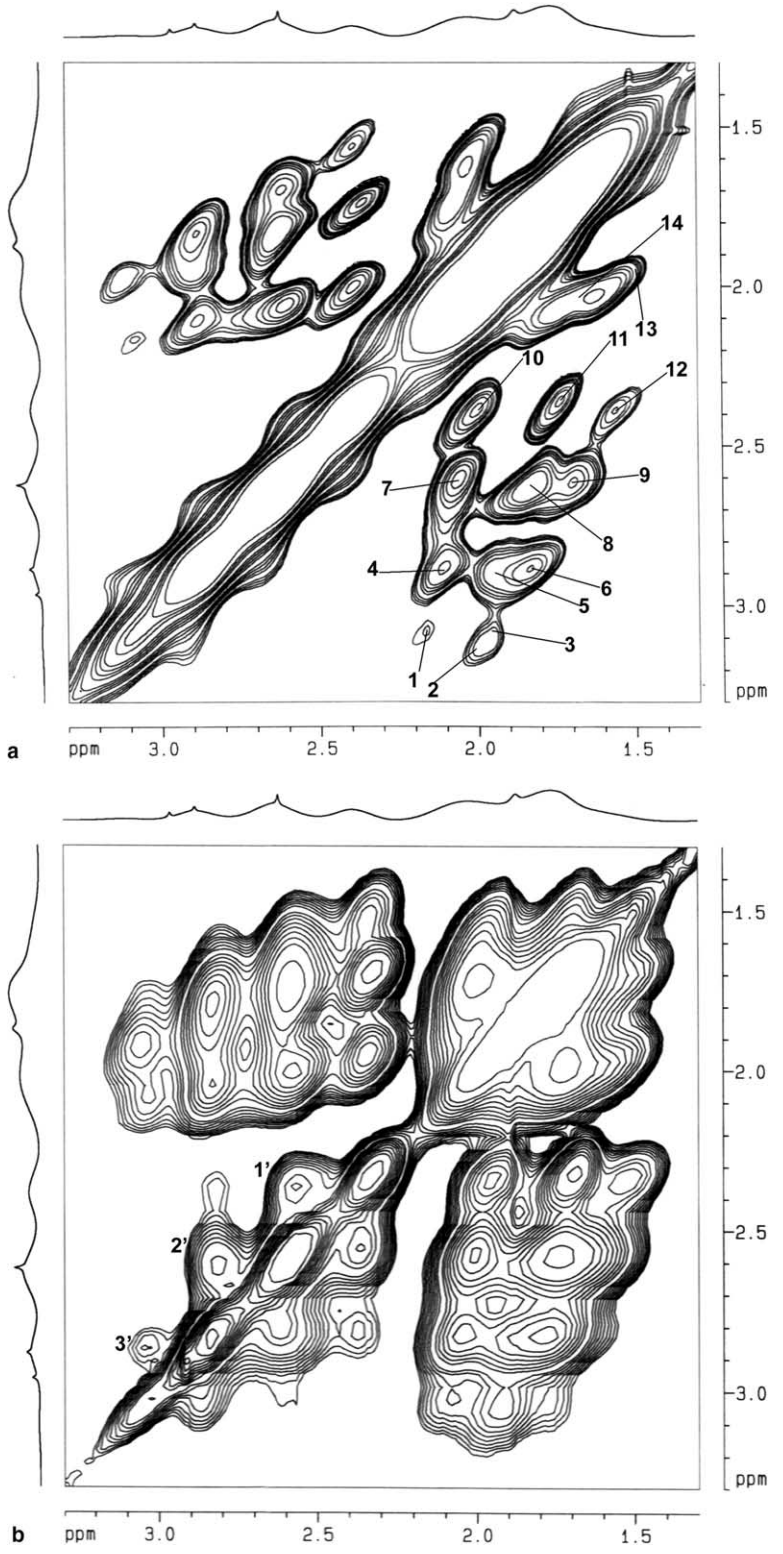


Fig. 4. (a) 2D TOCSY NMR spectrum of acrylonitrile/methyl acrylate copolymer ($F_A = 0.36$) in $CDCl_3$ (mixing time = 4 ms). (b) 2D TOCSY NMR spectrum of acrylonitrile/methyl acrylate copolymer ($F_A = 0.36$) in $CDCl_3$ (mixing time = 80 ms).

correlation (HSQC) of A/M copolymer [shown in Fig. 2(a) $F_A = 0.36$, (b) $F_A = 0.26$]. Methine carbons of A unit shows compositional as well as configurational sensitivity. The crosspeaks at (1) 27.57/3.06, ($1^{\#}$) 28.13/3.13, ($1^{\#\#}$) 28.67/3.10, (2) 28.00/2.89, (3) 27.39/2.86, (4) 27.92/2.67 ppm were assigned to AmAmA, AmArA, ArArA, AmAM, ArAM, MAM triads respectively on the basis of HSQC spectrum of poly(acrylonitrile). The methine carbon signals of M unit showed compositional sensitivity. The crosspeaks at (5) δ 41.15/2.85, (6) δ 41.15/2.63, (7) δ 41.28/2.39 ppm were assigned to AMA, AMM, MMM respectively (shown in Table 1).

3.3. ^1H NMR studies

The complex ^{1}H NMR spectrum was assigned tentatively from one to one correlation between carbon and proton signals. The proton spectrum along with complete assignments is shown in Fig. 3 ($F_A = 0.36$). In the ^{1}H NMR spectrum, the methine protons of acrylonitrile and methyl acrylate were assigned around δ 2.25–3.15 ppm and the methylene protons of A/M units resonate around δ 1.60–2.10 ppm. The methine proton signals of acrylonitrile and methyl acrylate show up as multiplet, indicating that they are compositionally sensitive. These signals were then assigned with the help of TOCSY spectrum.

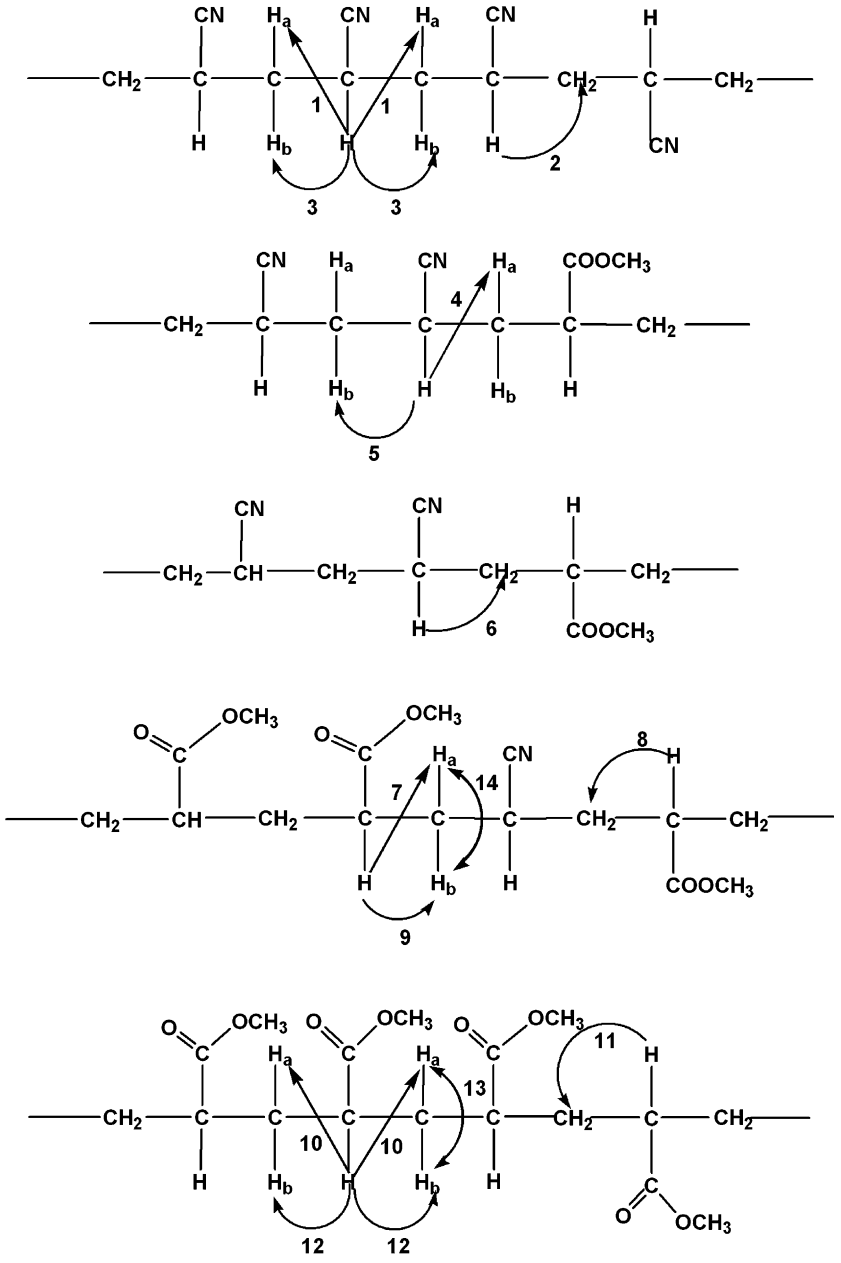
3.4. 2D TOCSY

In order to establish various connectivities in the copolymer chain, the TOCSY spectra were recorded. In the TOCSY spectrum apart from the direct coupling, relayed couplings were also seen. At shorter mixing time, there is direct coupling (AM spin type) whereas at higher mixing time there is relay coupling (AMX spin type) through magnetization transfer. Fig. 4 shows 2D TOCSY spectra of A/M copolymer recorded in $CDCl_3$ with different mixing time (a) 4 ms and (b) 80 ms. The vicinal couplings of methine protons (in both A and M centered triads) with methylene protons (in AA, MM and AM dyads in various compositional and configurational sequences) were assigned in the TOCSY spectra (mixing time, 4 ms).

In the *low mixing time* (4 ms) the crosspeaks centered at (1) δ 3.09/2.17 and (3) δ 3.09/1.949 ppm were assigned due to the coupling between the methine and methylene protons in meso configuration (a and b respectively) and the crosspeak centered at (2) δ 3.14/1.99 (2) ppm is assigned due to the coupling between methine and methylene protons in the racemic configuration of AAA triad. In the AAM triad, central methine proton found to be coupled (^3J) with two types of methylene protons (A and M type) at (4) δ 2.87/2.11, (5) δ 2.88/1.94 and (6) δ 2.88/1.83 ppm assigned to AmAmM(H_a), AmAM(H_b), AArM triads respectively. The crosspeaks at (7) δ 2.60/2.06 (MMmA), (8) δ 2.62/1.83 (MMrA), (9) δ 2.62/1.69 (MMmA) ppm were due to the three bond coupling between the methine proton and methylene protons of A and M types. The crosspeaks (10) and (12) at δ 2.39/2.00, δ 2.39/1.55 ppm were due to the meso configuration (a and b respectively) and the crosspeak (11) at δ 2.36/1.73 ppm was assigned to the racemic configuration of MMM triad sequence. The crosspeak at (13) δ 2.00/1.55 and (14) 2.08/

Table 2
TOCSY (mixing time = 4 ms) ^{1}H–^{1}H shift correlation in acrylonitrile/methyl acrylate copolymer

Peak no.	Type of proton (ppm)	Coupled to (ppm)
	Vicinal coupling between	
1	CH of AAA (3.09)	CH_2 of AmA(H_a) (2.17)
2	CH of AAA (3.14)	CH_2 of ArA (1.99)
3	CH of AAA (3.09)	CH_2 of AmA(H_b) (1.95)
4	CH of AAM (2.87)	CH_2 of AmM(H_a) (2.11)
5	CH of AAM (2.88)	CH_2 of AmA(H_b) (1.94)
6	CH of AAM (2.88)	CH_2 of ArM (1.83)
7	CH of MMA (2.60)	CH_2 of AmM(H_a) (2.06)
8	CH of MMA (2.62)	CH_2 of MrA (1.83)
9	CH of MMA (2.62)	CH_2 of MmA(H_b) (1.69)
10	CH of MMM (2.39)	CH_2 of MmM (H_a) (2.00)
11	CH of MMM (2.36)	CH_2 of MrM (1.73)
12	CH of MMM (2.39)	CH_2 of MmM(H_b) (1.55)
	Geminal coupling between	
13	H_a (2.00) coupling with H_b (1.55) (methylene protons of MM)	
14	H_a (2.08) coupling with H_b (1.70) (methylene protons of MA)	



Scheme 1. Interactions between methine and methylene protons which were observed with the help of TOCSY.

1.70 ppm shows two bond coupling between H_a and H_b of methylene protons of MM and AM dyads. These assignments were done by comparing TOCSY NMR spectra of the copolymers of various compositions and that of the corresponding homopolymers (Table 2 and Scheme 1).

The higher order sequences in the A/M copolymers were assigned with the help of the *higher mixing time*

Table 3
TOCSY (mixing time = 80 ms) ^1H–^1H shift correlation in acrylonitrile/methyl acrylate copolymer

Peak no.	Peak position (ppm)	Peak assignment (relay coupling between)
1′	2.56/2.35	MMMA (AMM–MMM)
2′	2.81/2.60	AAMM (AAM–AMM)
3′	3.04/2.86	AAAM (AAA–AAM)

TOCSY (80 ms) spectrum (Fig. 4(b)). The crosspeak at (1′) δ 2.56/2.35 ppm shows a relayed coupling between the methine protons of MMM and MMA triads, thus accounting for MMMA tetrad. The crosspeak at (2′) δ 2.81/2.60 ppm was assigned to AAMM which is showing relay coupling between the methine protons of AAM and MMA traids. The methine proton of AAA (δ 3.04 ppm) show a relayed coupling with methine proton of AAM (δ 2.86 ppm) thus accounting for AAAM (3′) tetrad (shown in Table 3).

3.5. HMBC

Heteronuclear multiple-bond correlation (HMBC) spectroscopy involves proton–carbon connectivities through coupling over two or three bonds and is valuable for the peak assignments of non-protonated carbons, such as quaternary, nitrile and carbonyl carbons [16,38–41]. Various triads in the nitrile and the carbonyl region of A/M copolymers assigned tentatively through ID NMR by comparing $^{13}C\{^1H\}$ NMR spectra of the copolymers of the various compositions and that of the corresponding homopolymers were correlated to the proton signals. In the HMBC spectra the triads of the carbonyl and nitrile region show coupling with the methine and the methylene region of A/M copolymer which were assigned with the help of 2D HSQC and 2D TOCSY.

Table 4
HMBC data showing correlation between carbonyl carbon and proton in acrylonitrile/methyl acrylate copolymer

Peak no.	Type of carbonyl carbon (ppm)	Coupled to proton (ppm)
1	MMM (174.88)	CH(M) (2.38)
2	MMM (174.85)	CH_2(MmM)(H_a) (1.99)
3	MMM (174.88)	CH_2(MrM) (1.73)
4	MMM (174.72)	CH_2(MmM)(H_b) (1.56)
5	MMA (173.90)	CH(M) (2.59)
6	MMA (174.04)	CH_2(AmM)(H_a) (2.07)
7	MMA (174.14)	CH_2(MrA) (1.82)
8	MMA (174.17)	CH_2(MmA)(H_b) (1.67)
9	AMA (173.50)	CH_2(ArM) (1.85)

The HMBC spectrum of acrylonitrile–methyl acrylate copolymer ($F_A = 0.36$) in Fig. 5 shows the

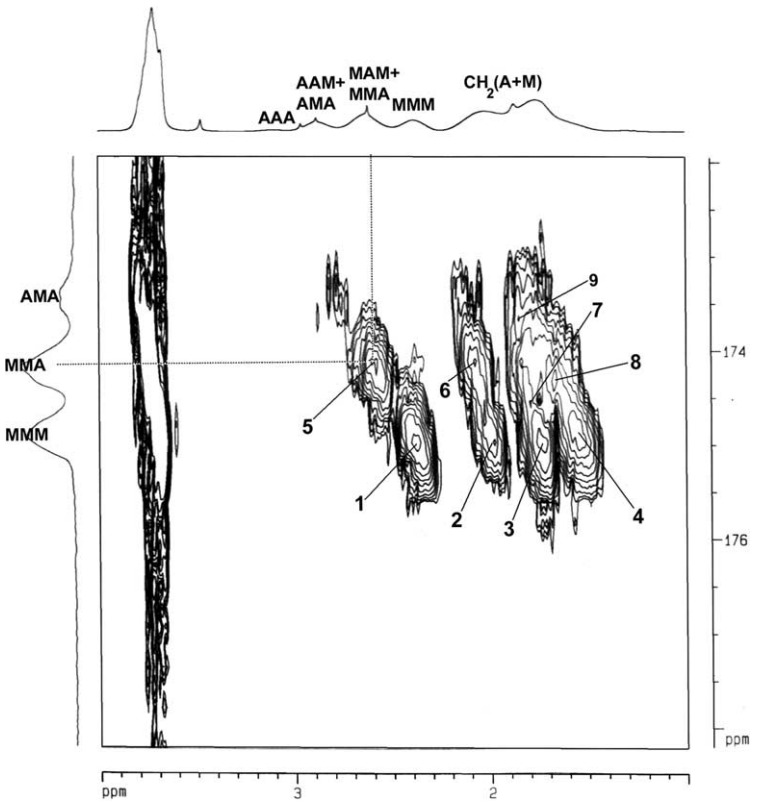
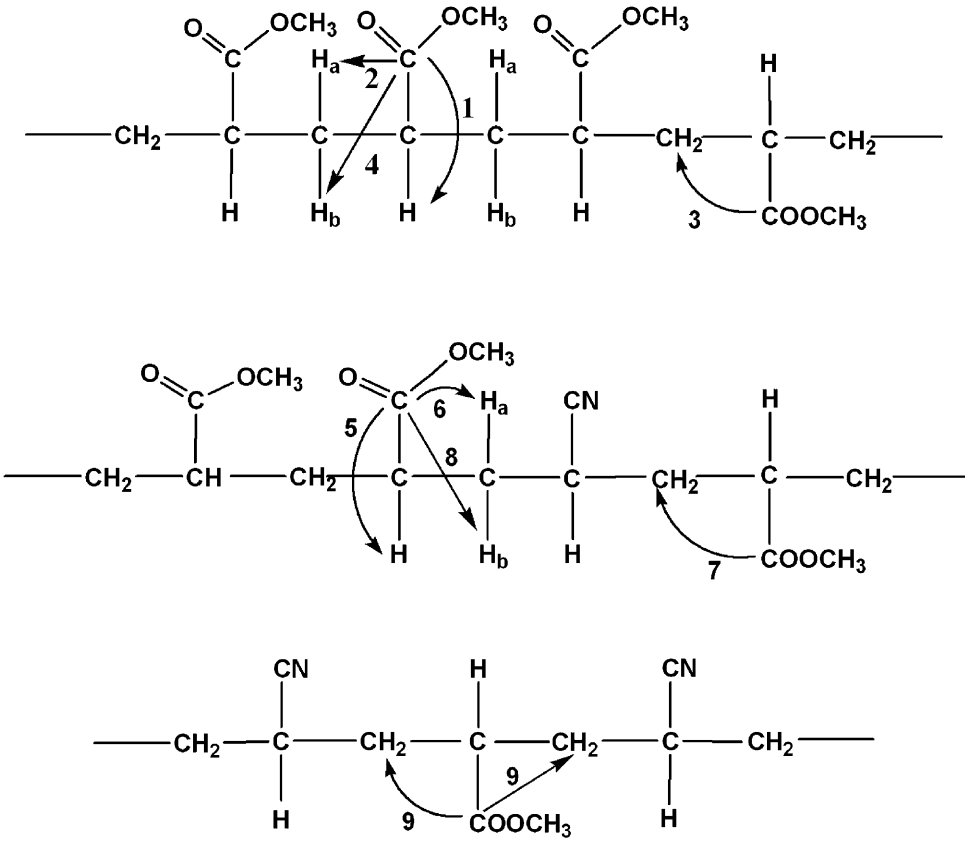


Fig. 5. 2D HMBC NMR spectra of acrylonitrile/methyl acrylate showing the interactions between the carbonyl carbon and proton ($F_A = 0.36$) in $CDCl_3$.



Scheme 2. Various interactions between carbonyl carbon and protons which were observed with the help of HMBC.

correlation between carbonyl group and methine/methylene protons. The carbonyl carbon signal at δ 174.88, 174.85, 174.88, 174.72 ppm shows the correlation to (1) MmMmM (2.38 ppm) methine, and (2) MmM(H_a) (1.99 ppm), (3) MrM (1.73 ppm), (4) MmM(H_b) (1.56 ppm) methylene proton signals while the carbonyl carbon at 173.90 ppm shows correlation with the methine of M unit, (5) MMA (2.59 ppm). The crosspeaks at (6) 174.04/2.07 ppm, (7) 174.14/1.82 ppm, (8) 174.17/1.67 ppm show the interaction of carbonyl carbons with the methylene protons of MmA(H_a), MrA, MmA(H_b) respectively. Carbonyl region at δ 173.50 ppm shows correlation to ArM at 1.85 (9) ppm of the methylene proton region (Table 4 and Scheme 2).

Fig. 6(a) and (b) shows the HMBC spectra of the copolymers showing the long range coupling of the nitrile carbon with the proton axis. The crosspeak (1) (120.11/1.72 ppm) and (2) (120.36/1.87 ppm) were assigned to the coupling of nitrile carbons with the methylene protons in MmA(H_b) and MrA respectively. Crosspeak (3) (120.29/2.02 ppm), (4) (119.53/2.08 ppm) was assigned to the couplings of the nitrile carbon (MAM, MAA) with the methylene protons of AmM-(H_a), AmM(H_a) respectively. Nitrile at 119.52 ppm shows coupling with (5) AAM (2.88 ppm). The crosspeak (6) 119/3.06 ppm was assigned to the couplings of the nitrile carbons with AmAmA (Table 5 and Scheme 3).

4. Conclusions

The value of reactivity ratios obtained by Kelen–Tudos method (KT) and non-linear error in variable method (RREVM) were found to be $r_A = 1.21 \pm 0.11$, $r_M = 0.90 \pm 0.08$ and $r_A = 1.11$, $r_M = 0.84$ respectively. The values of reactivity ratios indicate that there is random placement of two monomers along the copolymer chain. The structure of the acrylonitrile/methyl acrylate copolymer was analyzed using one- and two-dimensional NMR spectroscopy. With the help of HSQC experiment, the methine carbon and proton resonances of A and M units were assigned upto the triad level. TOCSY studies showed configurational sensitivity of methylene protons which further coupled with the

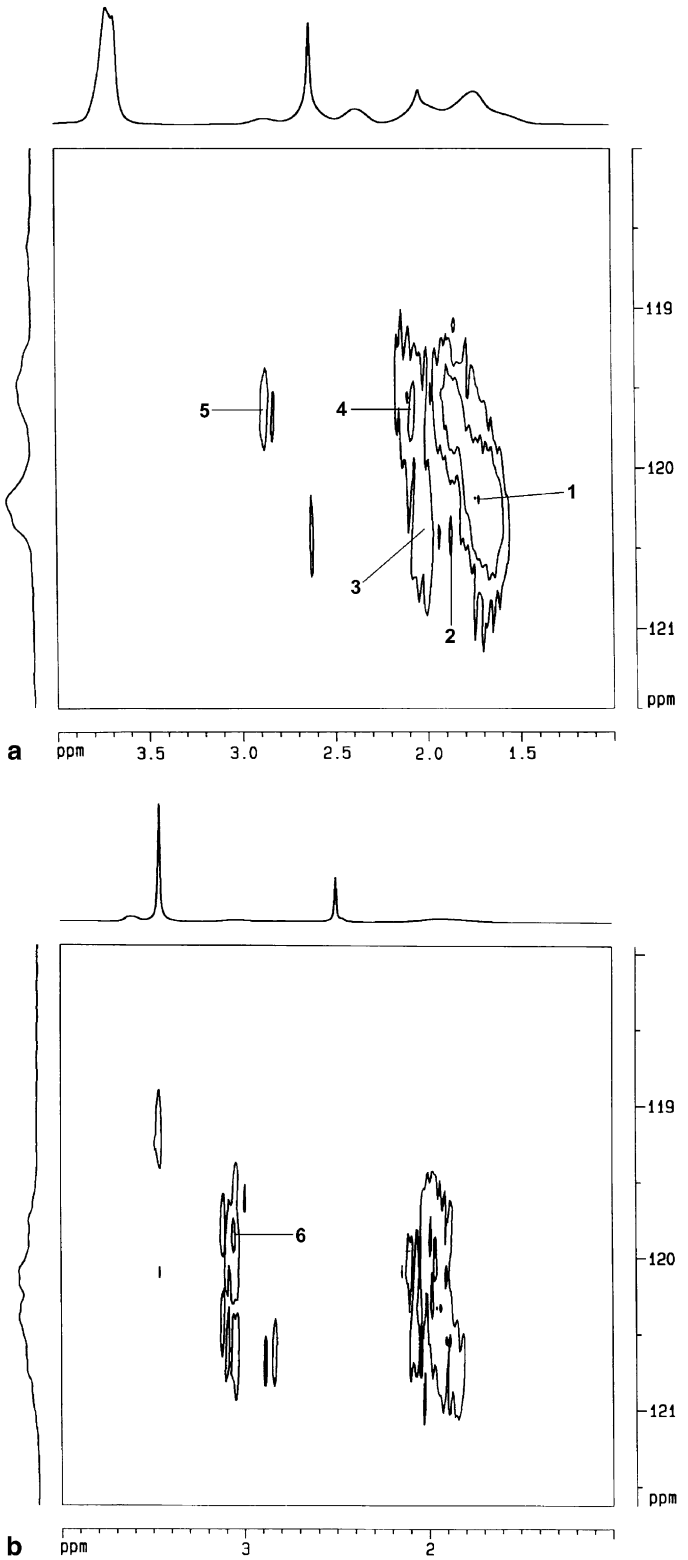
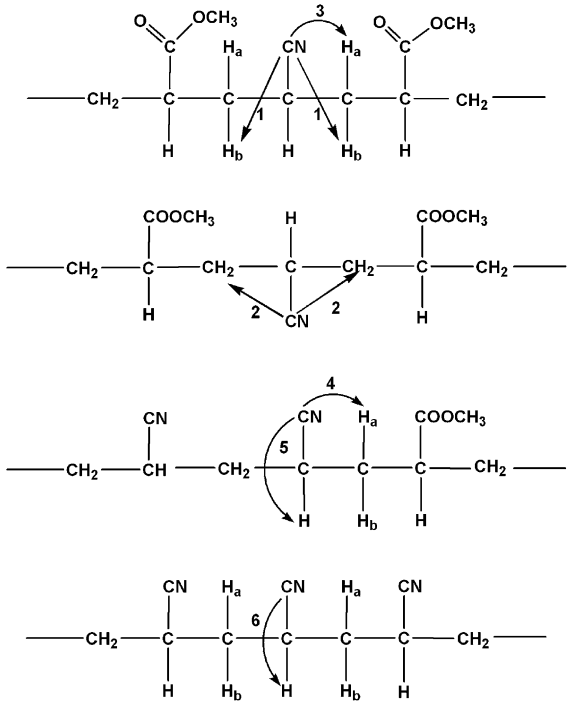


Fig. 6. 2D HMBC NMR spectra of acrylonitrile/methyl acrylate showing the interactions between the nitrile carbon and proton, (a) $F_M = 0.28$ (in DMSO), (b) $F_A = 0.26$ (in $CDCl_3$).

Table 5
HMBC data showing correlation between nitrile carbon and proton in acrylonitrile/methyl acrylate copolymer

Peak no.	Type of nitrile carbon (ppm)	Coupled to proton (ppm)
1	MAM (120.11)	$CH_2(MmA)(H_b)$ (1.72)
2	MAM (120.36)	$CH_2(MrA)$ (1.87)
3	MAM (120.29)	$CH_2(AmM)(H_a)$ (2.02)
4	MAA (119.53)	$CH_2(AmM)(H_a)$ (2.08)
5	MAA (119.52)	CH(A) (2.88)
6	AAA (119.77)	CH(A) (3.06)



Scheme 3. Various interactions between nitrile carbon and protons which were observed with the help of HMBC.

methine protons of A and M centered triads. TOCSY experiment confirmed the assignments of HSQC spectrum. HMBC experiment showed carbonyl and nitrile carbon couplings with the methine and methylene protons and confirms the assignments done by HSQC and TOCSY.

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