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Complete Spectral Assignments and Microstructures of Photopolymerized Acrylonitrile/Methacrylic Acid Copolymers by NMR Spectroscopy

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ABSTRACT: Copolymers of acrylonitrile/methacrylic acid were prepared by photopolymerization using the uranyl ion as a photosensitizer. The comonomer reactivity ratios, determined by both Kelen–Tüdös (KT) and nonlinear error in variables (EVM) methods are $r_A = 0.135 \pm 0.04$ and $r_M = 3.618 \pm 0.49$. The microstructure was obtained in terms of the distribution of A- and M-centered triad sequences from ^{13}C - $\{^1\text{H}\}$ NMR spectra of the copolymers. Homonuclear 2D TOCSY NMR was used to simplify the complex ^1H spectra of A/M copolymers in terms of configurational/conformational sequences. The triad concentration calculated from Monte Carlo simulations (MC) gave good agreement with the triad concentration determined from NMR spectroscopy. MC simulation was also used to study the effect of the degree of polymerization on triad fractions.

Introduction

^{13}C NMR spectroscopy in solution has been used as a powerful experimental technique to determine the intramolecular (sequence distribution and tacticity) and intermolecular (chemical composition and molar mass distribution) chain structures of vinyl copolymers,¹ as they supply the information about the polymerization process. A few authors have investigated the copolymerization mechanism of acrylonitrile with methacrylic acid. Makushka et al.² studied the copolymerization of acrylonitrile and methacrylic acid in DMSO at 70 °C and calculated the terminal model reactivity ratios of $r_A = 0.25$ and $r_M = 0.75$. They also calculated the penultimate reactivity ratio from the triad fractions and found that there is a significant penultimate group effect for the methacrylic acid chain end radical. O'Donnell et al.³ investigated the copolymerization in bulk at 60 °C to assess the copolymerization mechanism and reported the terminal model reactivity ratios as $r_A = 0.163$ and $r_M = 3.14$. They could not differentiate between the terminal model and the penultimate model. O'Donnell et al.¹² also reported the ^{13}C NMR spectral assignments of acrylonitrile/methacrylic acid copolymers using DEPT and 2D HETCOR experiments.

Earlier, we have reported the microstructure of acrylonitrile/alkyl acrylate^{4–6} by ^{13}C NMR spectroscopy. In this article, we report the copolymerization mechanism of acrylonitrile/methacrylic acid copolymers prepared by photopolymerization at room temperature using the uranyl ion as photoinitiator.⁷ The reactivity ratios of the comonomers were calculated using the nonlinear least squares error in variable method (EVM).⁸ The monomer composition and triad sequence distribution obtained from NMR are compared with those calculated from statistical models using the reactivity ratios determined using the EVM program. The highly complex ^1H NMR spectra of these copolymers have been completely assigned to different compositional/configurational sequences with the aid of 2D COSY and TOCSY experiments. This type of result has not been reported so far.

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The Monte Carlo (MC) simulation method⁹ is used to model the changes in copolymer sequence behavior during the course of the polymerization. The triad fractions calculated from MC simulations are compared with experimental (NMR) data. Further MC simulations are used to predict the variation of triad fractions as a function of the degree of polymerization.

Experimental Section

Acrylonitrile and methacrylic acid (Merck, Germany) were distilled under reduced pressure and stored below 5 °C. Uranyl nitrate was mixed with the monomer at different molar feed ratios and polymerization was carried out at room temperature.⁷ The percent conversion was kept below 10% by precipitating the copolymers in methanol. The copolymers were further dissolved in dimethyl sulfoxide (DMSO) and reprecipitated in methanol.

The copolymer composition was determined by estimation of the carboxylic (COOH) group by titration and by percent nitrogen of the copolymers. The C, H, and N analyses were done on a Perkin-Elmer 240 C elemental analyzer instrument.

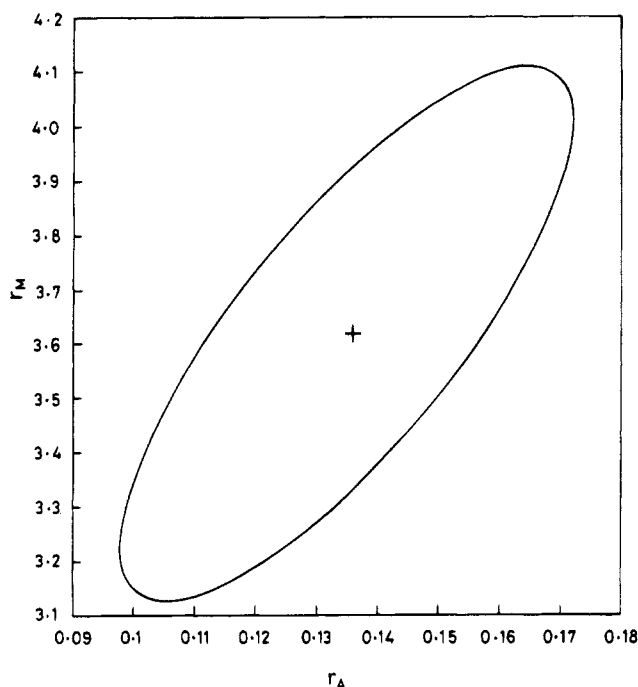
^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Varian 300 MHz spectrometer operating at 300 and 75 MHz, in DMSO- d_6 at 100 °C. The ^1H - ^1H 2D TOCSY experiment using the standard pulse sequence^{15,16} was carried out on a 500 MHz (Bruker) spectrometer at 100 °C in DMSO- d_6 . The mixing time used for this experiment was 31.5 ms. The details of recording the spectra and Lorentzian shape curve fitting have been described elsewhere.^{4–6} All regressions converged to $\chi^2 < 1$.

Results and Discussion

Reactivity Ratio Determination. The compositions of acrylonitrile (A)/methacrylic acid (M) copolymers were determined through estimation of the COOH group by titration. The copolymer composition was also determined by nitrogen analyses, and results obtained by both methods are in agreement with each other. Table 1 shows the comonomer mole fractions in the feed and in the copolymer. The initial estimate of reactivity ratios was done by the Kelen–Tüdös (KT) method.¹⁰ The values of reactivity ratios obtained from the KT plot are $r_A = 0.12 \pm 0.05$ and $r_M = 3.45 \pm 0.83$. These values along with the copolymer composition data were used to calculate the reactivity ratios using the EVM program. The errors in determining the monomer composition in feed and in copolymer were estimated to be

Table 1. Copolymer Composition for Acrylonitrile/Methacrylic Acid Copolymers (A/M)

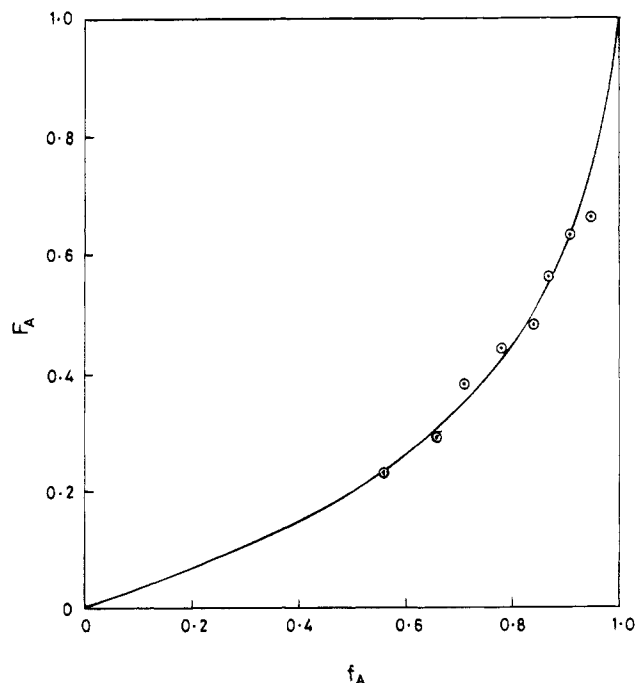
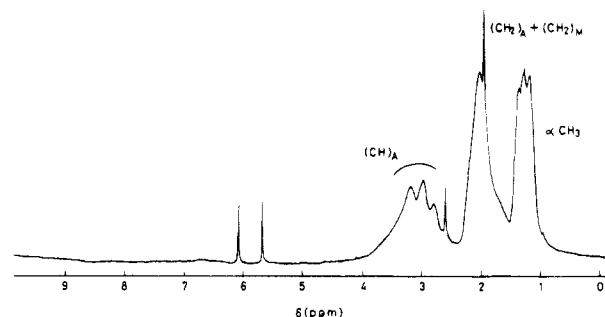
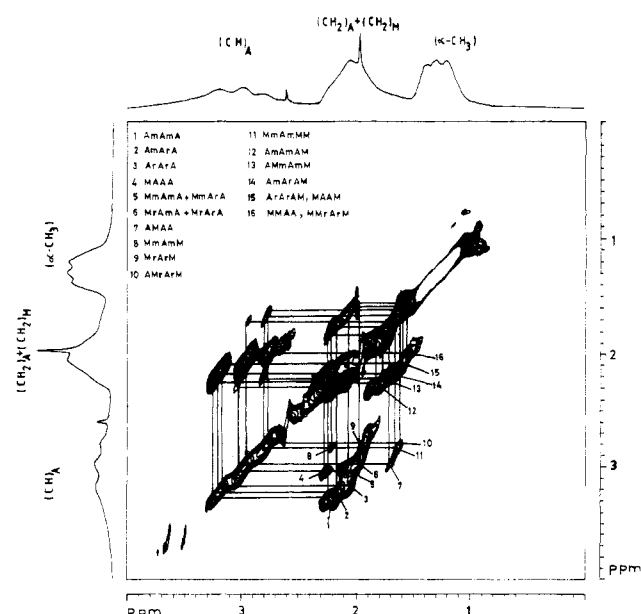
sample no.	feed mole fraction		copolymer composition ^a	
	f_A	f_M	F_A	F_M
1	0.95	0.05	0.66	0.34
2	0.91	0.09	0.63	0.37
3	0.87	0.13	0.56	0.44
4	0.84	0.16	0.48	0.52
5	0.78	0.22	0.44	0.56
6	0.71	0.29	0.38	0.62
7	0.66	0.34	0.29	0.71
8	0.56	0.44	0.23	0.77

^a From titration.**Figure 1.** 95% posterior probability contour for the acrylonitrile/methacrylic acid (A/M) comonomer pair.

1% and 3%, respectively. The values of reactivity ratios obtained from EVM are $r_A = 0.135 \pm 0.04$ and $r_M = 3.618 \pm 0.49$. These values of reactivity ratios are in good agreement with the reported values.³ A 95% joint confidence interval plot for the acrylonitrile/methacrylic acid comonomer pair is shown in Figure 1. The theoretical composition¹¹ curve (solid line) obtained from the copolymer composition equation using terminal model reactivity ratios ($r_A = 0.135$ and $r_M = 3.618$) along with experimentally determined copolymer compositions (symbols) is shown in Figure 2.

¹H NMR Studies. The ¹H NMR spectrum of the A/M copolymers ($F_A = 0.48$) in DMSO-*d*₆ at 100 °C is shown in Figure 3. In the case of the A/M copolymer, α -methyl ($-\text{CH}_3$)_M and methylene ($-\text{CH}_2$) protons are assigned around δ 0.9–1.4 and 1.5–2.4 ppm, respectively. The methine (CH) proton resonance (δ 2.6–3.3 ppm) shows a multiplet, indicating that it is sensitive toward the compositional sequence. The methine (CH) proton shows splitting based upon the triad sequence in the copolymer which is assigned as MAM (δ 2.6–2.84 ppm), AAM (MAA) (δ 2.84–3.06 ppm), and AAA (δ 3.06–3.3 ppm) from high to low field.

All the CH triad resonances further show tetrad sensitivity, which can be explained using TOCSY experiments. The 2D COSY spectrum clearly indicates that there are no substantial head to head or tail to tail linkages in the copolymer chain. In total correlated spectroscopy^{15,16} (TOCSY, also known as HOHAHA)

**Figure 2.** Theoretical composition curve obtained using reactivity ratios $r_A = 0.135$ and $r_M = 3.618$, along with experimentally determined copolymer composition (•).**Figure 3.** 500 MHz ¹H NMR spectrum of the acrylonitrile/methacrylic acid copolymer ($F_A = 0.44$).**Figure 4.** 500 MHz ¹H NMR 2D-TOCSY spectrum of the acrylonitrile/methacrylic acid copolymer ($F_A = 0.44$).

cross peaks between all the spins in a coupled system are observed. In the TOCSY spectrum, along with

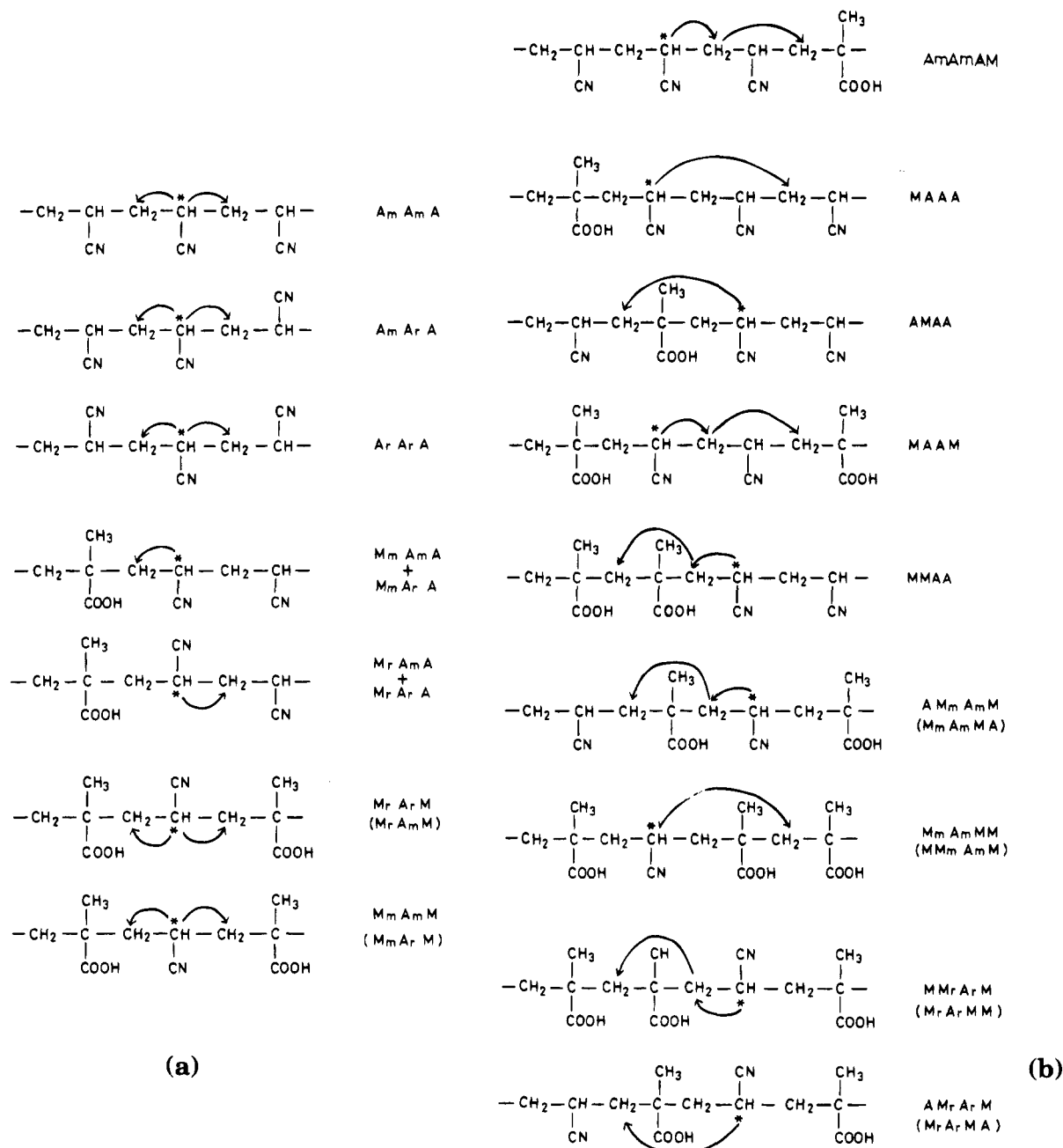


Figure 5. Structures of acrylonitrile-centered comonomer sequence for A/M copolymer.

COSY (three-bond) coupling, long distance (four-, five-bond) coupling can be seen depending on the mixing time. Figure 4 shows the 2D TOCSY spectrum of the A/M copolymer.

The COSY cross peaks which are present in the TOCSY spectrum are assigned as follows. The CH proton in AAA, MAA, and MAM triads is configuration sensitive. In the AAA triad, the CH proton shows three CH/CH₂, δ 3.28 ppm/ δ 2.25 ppm, δ 3.20 ppm/ δ 2.17 ppm, and δ 3.14 ppm/ δ 2.10 ppm, coupling cross peaks. These cross peaks, showing triad configurational sensitivity, are assigned as AmAmA, AmArA, and ArArA, as shown in Figure 5a. The methine proton of the MAA triad shows two CH/CH₂, δ 2.96 ppm/ δ 1.97 ppm and δ 3.03 ppm/ δ 2.10 ppm, coupling cross peaks which may be assigned to (MmAmA + MmArA) and (MrAmA + MrArA) (Figure 5a). Similarly in the MAM triad region, the methine proton shows two cross peaks, δ 2.82 ppm/ δ 2.20 ppm and δ 2.77 ppm/ δ 1.97 ppm, with methylene protons, corresponding to MmAmM and MrArM triad

sequences (Figure 5a) based on AmAmA and ArArA triads.

These protons further show tetrad conformational sensitivity. The tetrad sensitivity can be explained by 2D TOCSY experiments. In the AAA triad region, the CH (mm) proton at δ 3.28 ppm is coupled to the methylene proton at δ 2.25 ppm, which shows further four-bond coupling to another methylene proton at δ 1.81 ppm, as shown in Figure 5b, thus accounting for tetrad AmAmAM or MAmAmA. Similarly, the other two methine protons (mr and rr) also show tetrad sensitivity. The possible tetrad sequences are AmArAM (MAmArA) and ArArAM (MArArA). All these tetrads are part of the MAmAmAM, MAmArAM, and MArArAM pentads. However, other tetrad sequences for the AAA-centered triad were not distinguished because of overlapping.

In the MAA triad region, the CH protons at δ 3.03 and 2.96 ppm show five-bond coupling cross peaks with methylene protons at δ 2.28 and 1.72 ppm. These cross

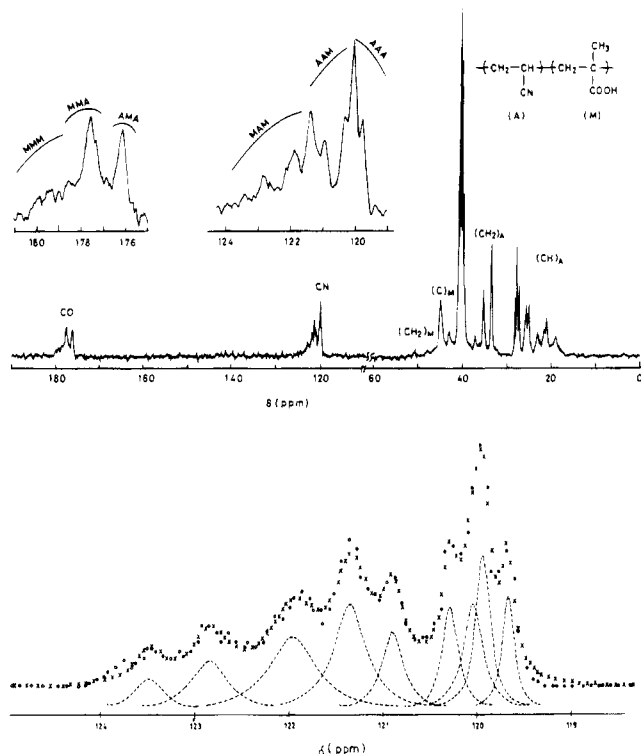


Figure 6. (a) 75 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the A/M copolymer ($F_A = 0.48$) along with the expanded carbonyl and nitrile carbons resonances in $\text{DMSO}-d_6$. (b) Component line fitting of the nitrile region of the A/M copolymer ($F_A = 0.48$): (○) experimental spectra; (×) fitted spectra; (---) component bands.

peaks are assigned as MAAA and AMAA, respectively (Figure 5b). The CH protons at δ 3.03 and 2.96 ppm show three-bond coupling with methylene protons at δ 2.10 and 1.97 ppm, which further show four-bond coupling with methylene protons at δ 1.57 and 1.54 ppm. These cross peaks are assigned to MAAM and MMAA tetrads. These tetrads are part of the AMAAA, AMAAM, MMAAA, and MMAAM pentad sequences of the MAA-centered triad.

Similarly in the MAM triad region, the methine protons at δ 2.82 and 2.77 ppm show three-bond and five-bond couplings with methylene protons at δ 2.20, 1.65 ppm and δ 1.97, 1.60 ppm, respectively. The five-bond CH/CH₂ coupling cross peaks are assigned to MmAmMM (MMmAmM) and MrArMA (AMrArM) tetrads (Figure 5b). The methylene protons at δ 2.20 and 1.97 ppm show further four-bond coupling with methylene protons at δ 1.76 and 1.54 ppm. These cross peaks are assigned to AMmAmM (MmAmMA) and MMrArM (MrArMM) tetrads. All these tetrads are part of MAM-centered pentads AMmAmMA, MMmAmMM, AMmAmMM, MMmAmMA, MMrArMA, AMrArMA, MMrArMM, and AMrArMM. Various TOCSY $^1\text{H}-^1\text{H}$ shift correlations with assignments are given in Table 2.

^{13}C NMR Studies. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the A/M copolymer ($F_A = 0.48$), in $\text{DMSO}-d_6$ at 100 °C, with all assignments is shown in Figure 6a.

The nitrile ($-\text{CN}$) and carbonyl ($>\text{C}=\text{O}$) carbon resonances showed multiplets, indicating that they are sensitive toward the compositional sequences and can be used for the assessment of the copolymerization mechanism. The expanded $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the nitrile ($-\text{CN}$) and carbonyl ($>\text{C}=\text{O}$) carbon resonances of the A/M ($F_A = 0.48$) copolymer are shown in Figure 6a. In PAN, the chemical shift difference within the

Table 2. TOCSY $^1\text{H}-^1\text{H}$ Shift Correlation with Assignments

peak no.	type of proton (ppm)	coupled to (ppm)	assignments
1	CH (3.28)	CH ₂ (2.25)	AmAmA
2	CH (3.20)	CH ₂ (2.17)	AmArA
3	CH (3.14)	CH ₂ (2.10)	ArArA
4	CH (3.03)	CH ₂ (2.28)	MAAA
5	CH (2.96)	CH ₂ (1.97)	MmAmA + MmArA
6	CH (3.03)	CH ₂ (2.10)	MrAmA + MrArA
7	CH (2.96)	CH ₂ (1.72)	AMAA
8	CH (2.82)	CH ₂ (2.20)	MmAmM (MmArM)
9	CH (2.77)	CH ₂ (1.97)	MrArM (MrAmM)
10	CH (2.77)	CH ₂ (1.60)	AMrArM (MrArMA)
11	CH (2.82)	CH ₂ (1.65)	MmAmMM (MMmAmM)
12	CH ₂ (2.25)	CH ₂ (1.81)	AmAmAM
13	CH ₂ (2.20)	CH ₂ (1.76)	AMmAmM (MmAmMA)
14	CH ₂ (2.17)	CH ₂ (1.72)	AmArAM
15	CH ₂ (2.10)	CH ₂ (1.57)	MAAM, ArArAM
16	CH ₂ (1.97)	CH ₂ (1.54)	MMAA, MMrArM

Table 3. Triad Compositions Calculated from NMR Spectra, Monte Carlo Simulations and the Alfrey-Mayo Model in Acrylonitrile/Methacrylic Acid (A/M) Copolymers (Final Conversion 5% for All Samples)

sample no.	feed mole fraction of A	triads	triad composition ^a		
			NMR $^{13}\text{C}\{^1\text{H}\}$	Alfrey-Mayo	Monte Carlo ^b
1	0.95	AAA	0.53	0.52	0.66
		AAM	0.39	0.40	0.30
		MAM	0.07	0.08	0.03
		MMM	0.00	0.03	0.01
		MMA	0.22	0.26	0.16
2	0.91	AMA	0.78	0.71	0.83
		AAA	0.33	0.33	0.43
		AAM	0.47	0.49	0.45
		MAM	0.19	0.18	0.12
		MMM	0.00	0.07	0.03
3	0.87	MMA	0.32	0.39	0.29
		AMA	0.68	0.54	0.68
		AAA	0.20	0.22	0.24
		AAM	0.50	0.50	0.49
		MAM	0.30	0.28	0.26
4	0.84	MMM	0.10	0.12	0.06
		MMA	0.45	0.45	0.38
		AMA	0.45	0.43	0.55
		AAA	0.19	0.17	0.15
		AAM	0.48	0.48	0.47
5	0.78	MAM	0.33	0.34	0.38
		MMM	0.18	0.17	0.10
		MMA	0.47	0.48	0.44
		AMA	0.34	0.35	0.46
		AAA	0.10	0.10	0.06
6	0.71	AAM	0.48	0.44	0.38
		MAM	0.42	0.46	0.56
		MMM	0.26	0.24	0.23
		MMA	0.47	0.50	0.50
		AMA	0.29	0.24	0.27
7	0.66	AAA	0.05	0.06	0.03
		AAM	0.43	0.37	0.29
		MAM	0.52	0.57	0.67
		MMM	0.28	0.36	0.41
		MMA	0.52	0.48	0.47
8	0.56	AMA	0.19	0.16	0.12
		AAA	0.06	0.04	0.02
		AAM	0.33	0.33	0.23
		MAM	0.61	0.63	0.75
		MMM	0.42	0.42	0.52
		MMA	0.46	0.45	0.40
		AMA	0.12	0.12	0.08
		AAA	0.03	0.02	0.01
		AAM	0.24	0.25	0.17
		MAM	0.73	0.73	0.82
		MMM	0.56	0.55	0.66
		MMA	0.38	0.38	0.30
		AMA	0.05	0.07	0.03

^a A- and M-centered triad fractions add up to unity. ^b MC simulation using $r_A = 0.135$ and $r_M = 3.618$.

resonance signals and the splitting pattern shows its sensitivity toward monomer sequence and cotacticity in

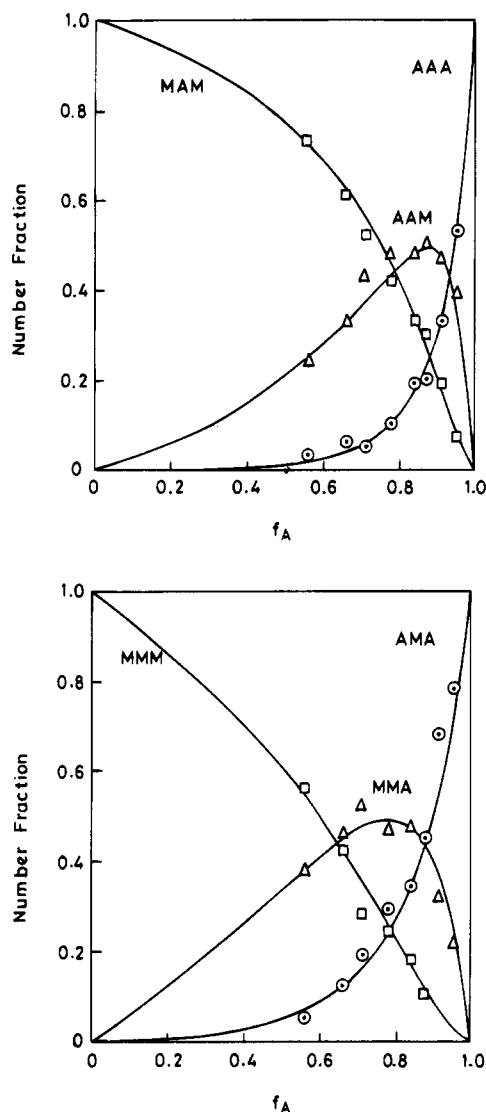


Figure 7. Variation of A- and M-centered triad fractions obtained from theoretical calculation (solid lines) and NMR spectroscopy (symbols) for the A/M copolymer plotted against feed mole fraction (f_A) of acrylonitrile.

the nitrile resonance. The signals around δ 119.0–120.2, 119.8–121.6, and 121.6–124.5 ppm are assigned to AAA, AAM(MAA), and MAM, respectively, on the basis of the variation in the spectra with copolymer composition. The overlapping peaks around δ 120.1 and 121.4 ppm were resolved, using a nonlinear least squares curve-fitting deconvoluting program (Figure 6b). The addition of the methacrylic acid to the AAA-centered triad causes a downfield shift in the position of AAM and MAM due to the deshielding effect of the carbonyl group in methacrylic acid.

In PMAA, the carbonyl ($>C=O$) carbon resonance is observed around δ 177.0–179.2 ppm. In the A/M copolymer, the carbonyl carbon resonance is split into three clear regions. As the concentration of acrylonitrile increases, resonance signals around δ 178.8–180.5 ppm decrease, while the upfield signal around δ 175.4–177.2 ppm increases. The signal around δ 177.2–178.8 ppm increases, goes through a maximum, and then decreases as the A unit concentration in the copolymer increases. The intensities of the three signals which change with the copolymer composition can be assigned as MMM, MMA(AMM), and AMA triad sequences from low to high field. This is due to the increase in electron density at the carbonyl carbon of the central M unit, which can be due to the diamagnetic shielding effect from the ani-

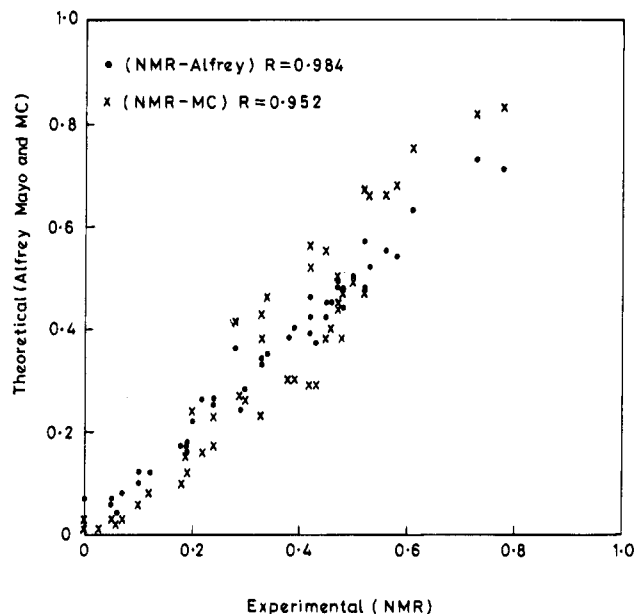


Figure 8. Correlation plot of theoretical (Monte Carlo and Alfrey-Mayo model) and experimental results (NMR) obtained on triad fractions for the A/M copolymer.

sotropy of the immediate $-CN$ group. The change in chemical shifts due to the monomer placements is larger than the cotacticity within the polymer chain.

The concentration of various A- and M-centered triads can be calculated from the relative areas of the resonance signals. These triad concentrations are the normalized areas of the respective resonance signals. Assuming the Alfrey-Mayo¹³ model (first-order Markov terminal model) to be valid at any moment of the polymerization reaction for these low-conversion copolymers, the triad concentration can be calculated using the terminal model reactivity ratio $r_A = 0.135$ and $r_M = 3.618$. A- and M-centered triad fractions along with those calculated using the Alfrey-Mayo model, using Harwood's program,¹⁴ are given in Table 3. There is good agreement between the calculated and the experimentally (NMR) determined triad fractions. Figure 7 shows the plots of normalized A- and M-centered triad concentration against the mole fraction of acrylonitrile. An increase in the concentration of acrylonitrile in the copolymers increases the fraction of the AAA triad while it decreases the fraction of the MAM triad. The AAM triad fraction first increases with the increase in feed mole fraction (f_A) of acrylonitrile, passes through a maximum, and then starts decreasing. Similarly, the MMM triad fraction decreases while the AMA triad fraction increases as the acrylonitrile concentration increases. The triad fraction (MMM) increases, goes through a maximum, and then decreases as f_A increases. The maximum fraction of AAM and MMA triads are at 0.87 and 0.79 mole fraction of acrylonitrile. In Figure 7 solid lines represent the theoretically calculated (Alfrey-Mayo) triad fraction whereas symbols represent the experimentally determined (NMR) triad fractions. It is clear that there is good agreement between the calculated and experimentally obtained triad fractions.

From the composition of various A- and M-centered triads, the conditional probability,^{7,11} $P_{M/A}$ and $P_{A/M}$, was calculated. The value of $P_{M/A}$ decreases linearly from 0.85 to 0.27 with the decrease in the content of M unit, while the value of $P_{A/M}$ increases linearly from 0.24 to 0.89 as the concentration of A unit increases in the copolymer. Using these values, the terminal model reactivity ratios (r_A and r_M) were calculated for indi-

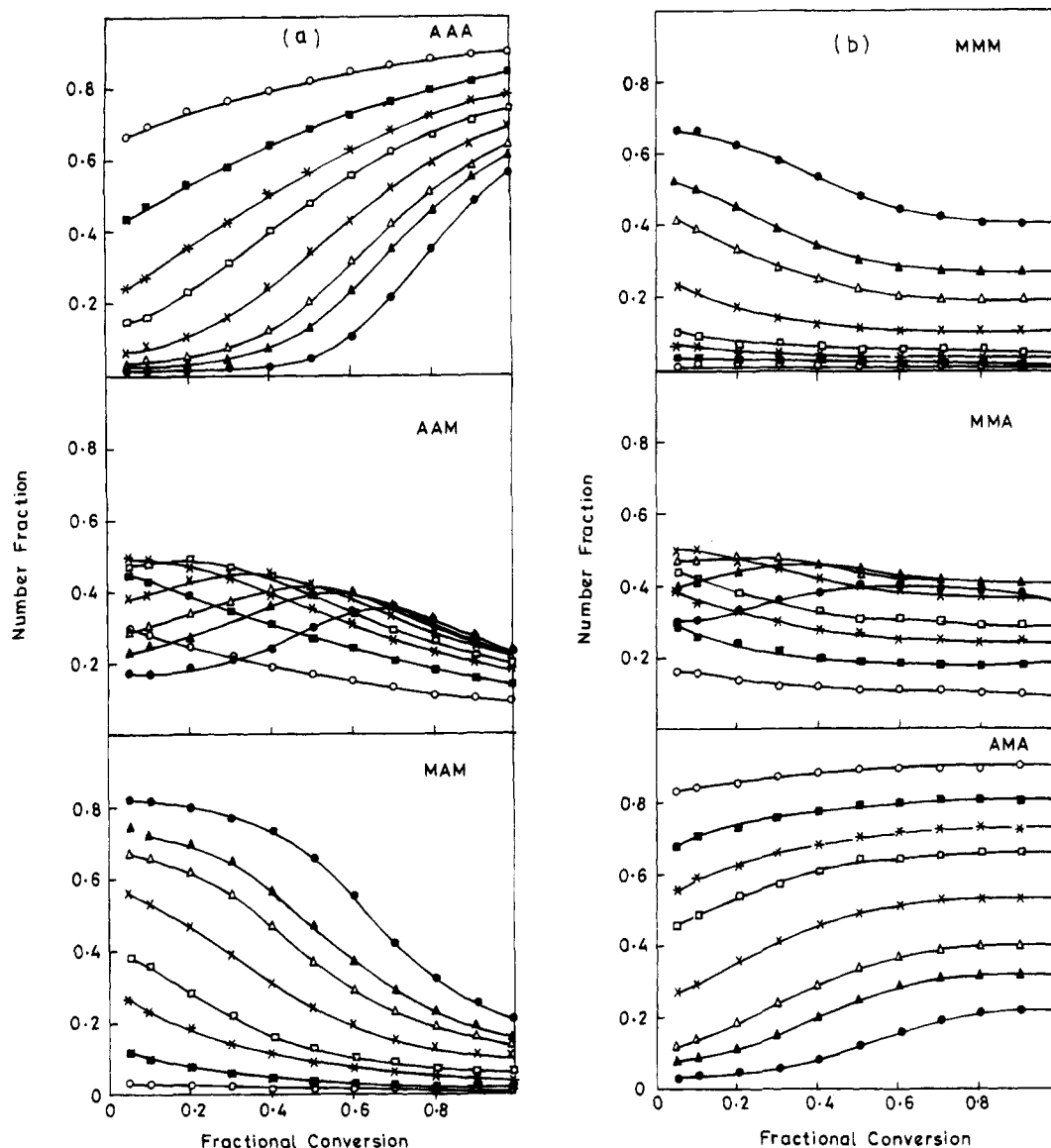


Figure 9. Variation of (a) A- and (b) M-centered triad fractions plotted as a function of fractional conversion for different feed mole fractions: $f_A = 0.95$ (○), $f_A = 0.91$ (■), $f_A = 0.87$ (*), $f_A = 0.84$ (□), $f_A = 0.78$ (×), $f_A = 0.71$ (△), $f_A = 0.66$ (▲), and $f_A = 0.56$ (●).

vidual copolymers. The average value of reactivity ratios obtained from triad composition are $r_A = 0.14 \pm 0.01$ and $r_M = 3.08 \pm 0.72$. The reactivity ratios obtained from the compositional data provide more accurate values than those obtained from the triad fraction.

Monte Carlo Simulation Studies. Monte Carlo (MC) simulation¹² is used to monitor the changes in copolymer sequence behavior during the course of the polymerization. MC simulation as adopted here is a probabilistic method to generate a polymer chain, where monomer addition to the growing chain is governed by the reactivity ratios. Once the copolymer chain was generated by simulation, various normalized diad, triad, and tetrad fractions were calculated. To improve the statistics, the above simulations were repeated 10 times with a different seed (random numbers) each time. This corresponds to averaging over 10 different copolymer chains generated under identical conditions.

Here, using the EVM reactivity ratios ($r_A = 0.135$ and $r_M = 3.618$), 10 copolymer chains were generated for each feed mole fraction (f_A). The copolymer sequence composition was then analyzed. Results are given in Table 3. A correlation plot was drawn (Figure 8) to compare the experimental data (NMR) with the calcu-

lated (Alfrey-Mayo) and simulated (MC) data. The correlation coefficient for NMR-Alfrey-Mayo data is $R = 0.983$, and that of NMR-MC is $R = 0.952$.

The MC simulation method can be used to calculate the triad concentration at various degrees of polymerization. Parts a and b of Figure 9 show the variation of the A- and M-centered triad concentration as a function of fractional conversion for different feed mole fractions. As the copolymerization progresses, the monomer with higher reactivity ratio (methacrylic acid) is consumed faster than the other monomer (acrylonitrile). Thus, at higher conversions, blocks of acrylonitrile, i.e. AAA, are formed. In Figure 9a, the AAA triad fraction is seen to increase as the conversion increases. As the feed mole fraction decreases, the triad fraction (AAA) increases only at higher conversions as methacrylic acid is consumed faster than acrylonitrile comonomer. The AAM triad fraction concentration first increases, goes through a maximum, and then decreases as the conversion increases. The maximum shifts toward higher conversion as (f_A) decreases. For extreme cases ($f_A < 0.3$ and $f_A > 0.9$) no maxima are seen; instead there is a steady increase or decrease of triad concentration as the degree of polymerization increases. The MAM triad fraction decreases as the fractional conversion increases. The

decrease is much sharper for lower feed mole fractions (f_A) at higher conversions. In Figure 9b, the MMM triad concentration decreases as the fractional conversion increases, as expected. The MMM triad concentration decreases sharply when f_A is low. For $f_A > 0.70$ the decrease is very small, while there is a significant decrease when $f_A < 0.70$, as conversion increases. The MMA triad concentration, for feed mole fractions lying between $0.70 > f_A > 0.30$, increases, goes through a maximum, and then decreases as the degree of polymerization increases. The maximum shifts toward higher conversion as f_A decreases. The third M-centered triad (AMA) concentration increases as fractional conversion increases. As f_A decreases, the AMA triad concentration increases at higher conversions, as the reactivity ratio of acrylonitrile comonomer is less than that of methacrylic acid.

Conclusions

The microstructures of the acrylonitrile/methacrylic acid copolymers have been investigated by NMR spectroscopy. The TOCSY experiments were used to make unambiguous assignments at the tetrad level of the methine proton in the ^1H spectra of the A/M copolymer. The reactivity ratios evaluated from composition data provide more accurate values than those evaluated from triad fractions. There is good agreement between the experimentally obtained (NMR) triad fractions and those calculated from theoretical models and MC simulations.

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