

Stereochemical and Compositional Assignments of *trans*-4-Methacryloyloxyazobenzene–Methyl Methacrylate Copolymers by One- and Two-Dimensional NMR Spectroscopy

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ABSTRACT: The microstructure of *trans*-4-methacryloyloxyazobenzene–methyl methacrylate copolymers prepared by solution polymerization process using AIBN as initiator is analyzed by one- and two-dimensional spectroscopy. Sequence distribution was calculated from the $^{13}\text{C}(^1\text{H})$ -NMR spectra of the copolymers. Comonomer reactivity ratios were determined using the Kelen–Tudos and the nonlinear error-in-variables methods are $r_A = 1.14 \pm 0.08$ and $r_M = 0.51 \pm 0.03$; $r_A = 1.13 \pm 0.1$ and $r_M = 0.50 \pm 0.04$, respectively. The sequence distribution of A- and M-centered triads determined from $^{13}\text{C}(^1\text{H})$ -NMR spectra of copolymer is in good agreement with triad concentration calculated from a statistical model. The 2-D heteronuclear single-quantum correlation and correlated spectroscopy (TOCSY) was used to analyze the complex ^1H -NMR spectrum. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3016–3025, 1999

Key words: *trans*-4-methacryloyloxyazobenzene/methyl methacrylate copolymers, 2-D NMR studies; sequence determination; photochromic polymers

INTRODUCTION

NMR spectroscopy is an indispensable tool for ongoing developmental research in the field of polymer science.^{1–5} With the aid of 2-D heteronuclear shift-correlation experiments and total-correlation spectroscopy (TOCSY), the higher order compositional and configurational sequences in the polymer chains can be easily assigned.

To the best of our knowledge, the detailed microstructure study of *trans*-4-methacryloyloxyazobenzene–methyl methacrylate (A–M) copolymers have not been reported so far. In this work an attempt has been made to report the stereochemical structure and sequence distribution of A–M copolymers by one- and two-dimensional NMR spectroscopy.

The ^1H -NMR spectrum of the copolymers is complex and has been interpreted with the help of 2-D heteronuclear single-quantum correlation (HSQC) NMR spectroscopy. The assignments in the ^1H -NMR spectrum are then used to confirm the interactions within the copolymer, using 2-D TOCSY NMR spectroscopy. The reactivity ratios of the comonomers have been calculated with the Kelen–Tudos (KT) and the nonlinear error-in-variable (EVM) methods,⁶ using the compositional data obtained from the ^1H -NMR spectrum. The A- and M-centered triad sequence distribution obtained from the $^{13}\text{C}(^1\text{H})$ -NMR spectra have been compared with those calculated from the first-order Markov model, using reactivity ratios determined from the EVM program.

EXPERIMENTAL

A series of *trans*-4-methacryloyloxyazobenzene–methyl methacrylate copolymers containing dif-

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Table I Copolymer Composition Data and Molecular Weight of the *trans*-4-Methacryloyloxyazobenzene/Methyl Methacrylate Copolymer by GPC Measurements

Sample	f_A	f_M	F_A	F_M	$\bar{M}_w (\times 10^{-4})$ (g/mol)	$\bar{M}_n (\times 10^{-4})$ (g/mol)	Polydispersity
AM1	0.1	0.9	0.17	0.83	2.9	2.6	1.1
AM2	0.2	0.8	0.30	0.70	3.3	2.5	1.3
AM3	0.3	0.7	0.40	0.60	4.0	2.7	1.5
AM4	0.4	0.6	0.50	0.50	7.3	3.8	1.9
AM5	0.5	0.5	0.58	0.42	7.7	3.8	2.0
AM6	0.6	0.4	0.68	0.32	8.6	4.4	2.0
AM7	0.7	0.3	0.75	0.25	8.3	4.0	2.1

f_A and f_M are the mole fractions of A- and M-comonomer, respectively, in feed. F_A and F_M are the mole fractions of A- and M-comonomers, respectively, in the copolymer. \bar{M}_w and \bar{M}_n are the weight and number average molecular weights of the copolymer, respectively.

ferent mole percents of A monomer in feed were prepared by solution polymerization, using AIBN (0.5%) as initiator in benzene at 65°C in a sealed tube under nitrogen atmosphere. The copolymer was precipitated using methanol. The percent conversion was kept below 10%. The copolymers were further dissolved in CHCl_3 and reprecipitated in methanol and vacuum-dried. The molecular weight of the copolymers was determined

from gel permeation chromatography using polystyrene as a narrow standard. The copolymer composition was determined from the ^1H -NMR spectrum.

NMR Measurements

The ^1H - and ^{13}C (^1H)-NMR spectra of copolymers were recorded under standard conditions at 25°C

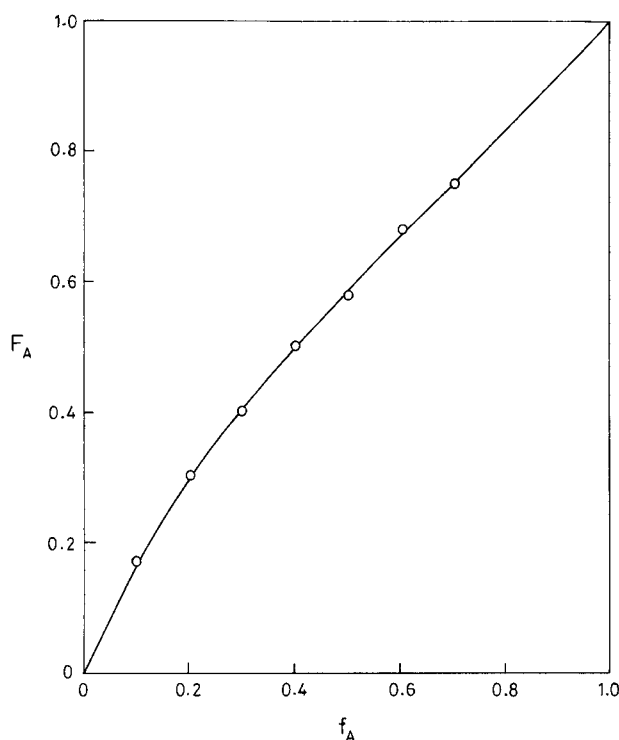


Figure 1 Theoretical composition curve obtained using reactivity ratios of $r_A = 1.13$ and $r_M = 0.50$ along with experimentally determined copolymer composition (o).

Table II The Compositional and Configurational Assignments of the A/M Copolymers from 2D-HSQC Spectrum

Peak No.	HSQC		Assignments
	^{13}C (ppm)	^1H (ppm)	
			CH_3
1	16.75	0.92	MMM
2	17.5	1.11	AMM
3	18.0	1.3	AMA
4	18.75	1.5	MAM
5	19.0	1.09	AAM
6	19.4	1.24	MAA
7	19.75	1.33	AAAAA
8	20.0	1.45	AAAAM
9	20.5	1.56	MAAAM
			CH_2
10	52.0	1.95–2.1	AM_mMM
11	53.7	2.02–2.2	MM_mMA
12	54.25	1.88–2.03	AM_mMA
13	52.7	2.1–2.28	AA_mMM
14	54.0	2.2–2.37	AA_mMA
15	54.5	1.75	MM_rMM
16	53.6	2.45	MAAM
17	54.5	2.5	MAAA
18	55.0	2.56	AAAA

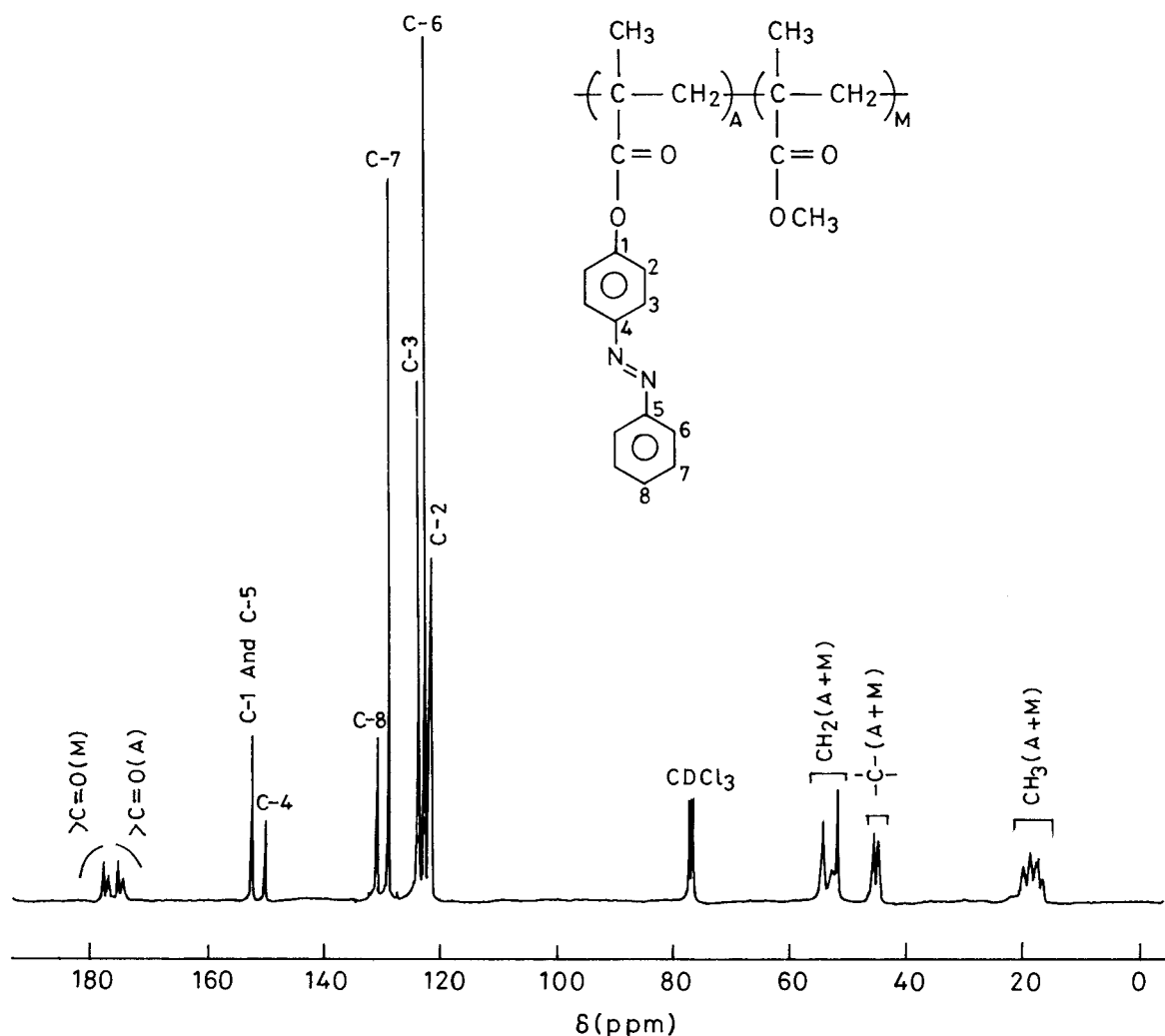


Figure 2 75-MHz $^{13}\text{C}(^1\text{H})$ -NMR spectra of the A-M copolymer ($F_A = 0.5$) in CDCl_3 .

in CDCl_3 on a Bruker 300-MHz spectrometer operating at 300 and 75.5 MHz, respectively. The 2-D ^1H - ^{13}C HSQC spectra were recorded under a standard pulse sequence, while the 2-D homonuclear ^1H - ^1H TOCSY experiment was carried out on a Bruker 300-MHz spectrometer at two different mixing times—4 and 80 ms. The details of the Lorentzian shape curve fitting have been described in our earlier publication.⁷ All regressions converged to $\chi^2 < 1$.

RESULTS AND DISCUSSIONS

Reactivity Ratios Determination

The composition of the A-M copolymers were determined from the ^1H -NMR spectrum. Table I shows the comonomer mole fractions in the feed

and in the copolymer. The copolymer composition data thus obtained were used to calculate the terminal model reactivity ratios by the Kelen-

Table III TOCSY ^1H - ^1H Shift Correlation with Assignments in A/M Copolymers

Peak No.	Type of Proton (ppm)	Coupled to (ppm)	Assignments
1	$\text{CH}_2(2.00)$	$\text{CH}_2(1.48)$	A MMM
2	$\text{CH}_2(2.07)$	$\text{CH}_2(1.54)$	A MMA
3	$\text{CH}_2(2.21)$	$\text{CH}_2(1.65)$	M A MM
4	$\text{CH}_2(2.28)$	$\text{CH}_2(1.71)$	A A MM
5	$\text{CH}_2(2.35)$	$\text{CH}_2(1.78)$	A A MA
6	$\text{CH}_2(2.45)$	$\text{CH}_2(1.88)$	A AAA
7	$\text{CH}_2(2.50)$	$\text{CH}_2(1.94)$	A A AM
8	$\text{CH}_2(2.55)$	$\text{CH}_2(2.00)$	M A AM

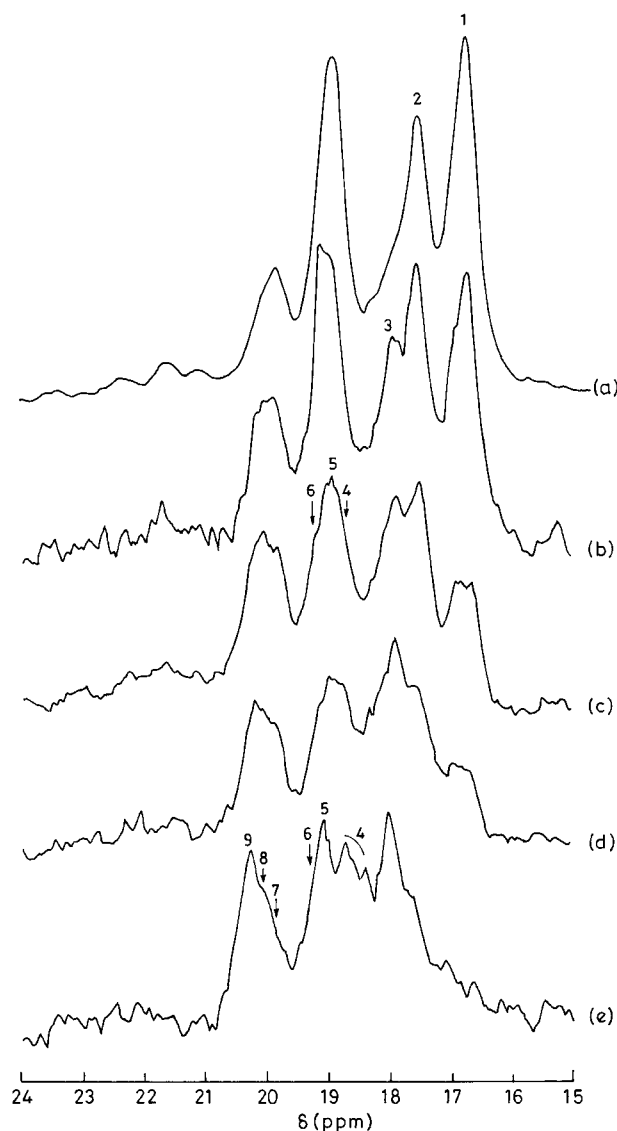


Figure 3 75-MHz $^{13}\text{C}(^1\text{H})$ -NMR spectra showing the methyl carbon signals of different copolymer compositions (F_A): (a) 0.3 (b) 0.4 (c) 0.5 (d) 0.58 (e) 0.68.

Tudos (KT) and the error-in-variables (EVM) methods, using the RREVM program. The values of the reactivity ratios obtained from the KT method are $r_A = 1.14 \pm 0.08$; $r_M = 0.51 \pm 0.03$. These values were used as the initial estimates in the RREVM program and obtained as $r_A = 1.13 \pm 0.10$ and $r_M = 0.5 \pm 0.04$.

The theoretical composition curve obtained from the copolymer composition equation using terminal model reactivity ratios ($r_A = 1.13 \pm 0.10$; $r_M = 0.5 \pm 0.04$) along with experimentally determined copolymer composition is shown in Figure 1. The experimental points are in agreement with the theoretically calculated ones, indicating

that the reactivity ratios obtained from the compositional data are reliable. The weight average and number average molecular weights of the copolymer are given in Table I.

Table IV Triad Fractions Calculated from NMR Spectra and Harwood's Terminal Model in A/M Copolymers

Sample No.	F_A	Triads	Triad Fractions	
			a	b
AM1	0.17	AAA	0.02	0.01
		AAM	0.24	0.20
		MAM	0.74	0.79
		MMM	0.71	0.67
		MMA	0.28	0.30
AM2	0.30	AMA	0.02	0.03
		AAA	0.07	0.05
		AAM	0.28	0.34
		MAM	0.65	0.61
AM3	0.40	MMM	0.42	0.45
		MMA	0.47	0.44
		AMA	0.11	0.11
		AAA	0.08	0.11
		AAM	0.47	0.44
AM4	0.50	MAM	0.45	0.45
		MMM	0.26	0.29
		MMA	0.51	0.50
		AMA	0.23	0.21
		AAA	0.18	0.18
AM5	0.58	AAM	0.46	0.49
		MAM	0.36	0.33
		MMM	0.17	0.18
		MMA	0.55	0.49
		AMA	0.28	0.33
AM6	0.68	AAA	0.31	0.28
		AAM	0.48	0.50
		MAM	0.21	0.22
		MMM	0.09	0.11
		MMA	0.49	0.45
AM7	0.75	AMA	0.42	0.44
		AAA	0.36	0.39
		AAM	0.52	0.47
		MAM	0.12	0.14
		MMM	0.05	0.06
		MMA	0.41	0.38
		AMA	0.54	0.56
		AAA	0.50	0.52
		AAM	0.43	0.40
		MAM	0.07	0.08
		MMM	0.03	0.03
		MMA	0.24	0.29
		AMA	0.73	0.68

a, triad fractions obtained from ^{13}C -NMR spectra of carbonyl carbon resonance signals; b, triad fractions calculated using $r_A = 1.13 \pm 0.1$ and $r_M = 0.5 \pm 0.04$ from Harwood's program.

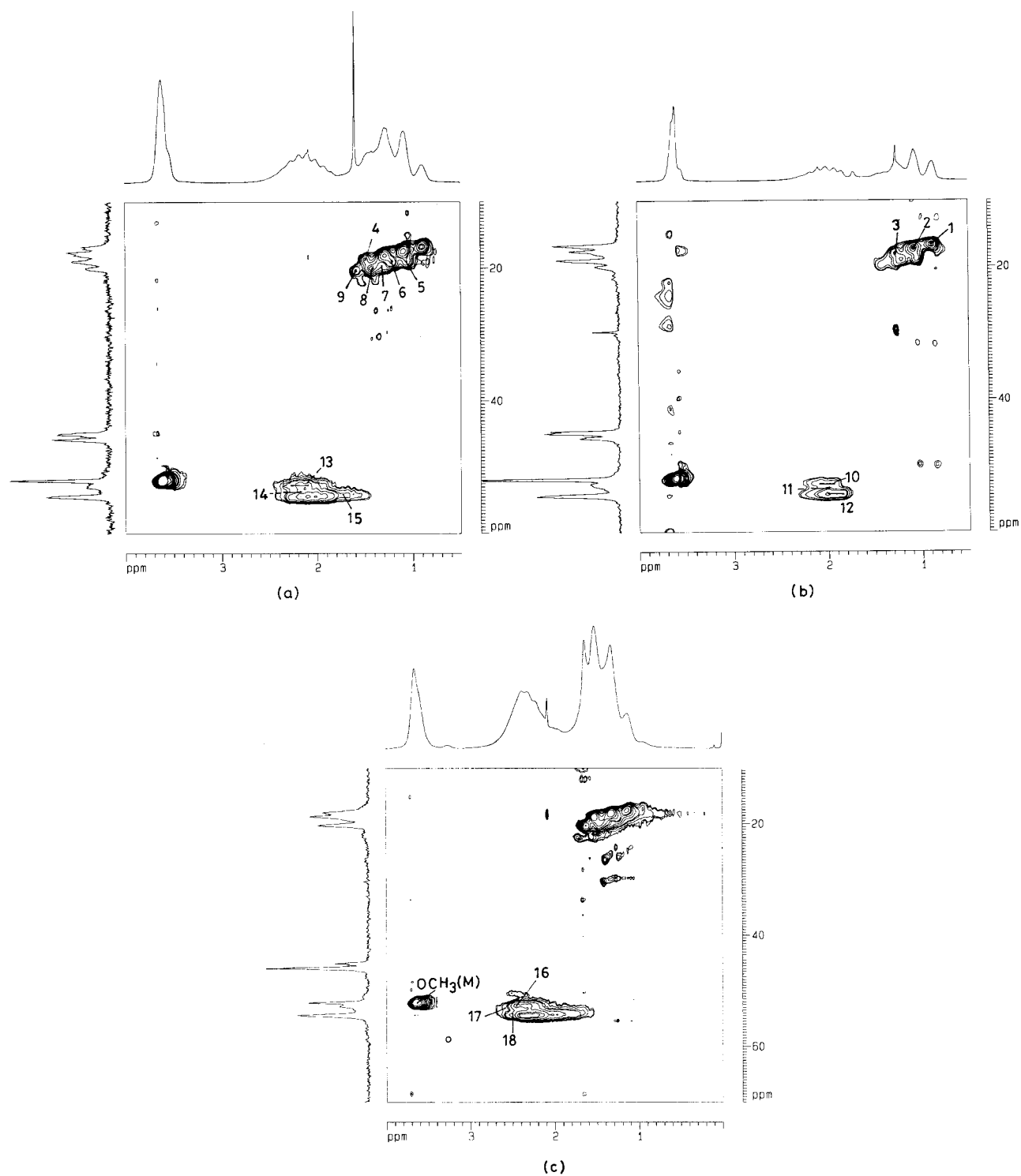


Figure 4 75-MHz 2-D-HSQC NMR spectra of the A-M copolymers: (a) $F_A = 0.5$ (b) $F_A = 0.17$ (c) $F_A = 0.75$ in CDCl_3 .

$^{13}\text{C}(\text{H})$ -NMR and ^1H -NMR Studies

The $^{13}\text{C}(\text{H})$ -NMR spectra of the A-M copolymer ($F_A = 0.5$) is shown in Figure 2 along with signal

assignments. The assignments of aromatic carbon resonance of A-monomeric units have been reported in previous papers.^{8,9} The methyl, quater-

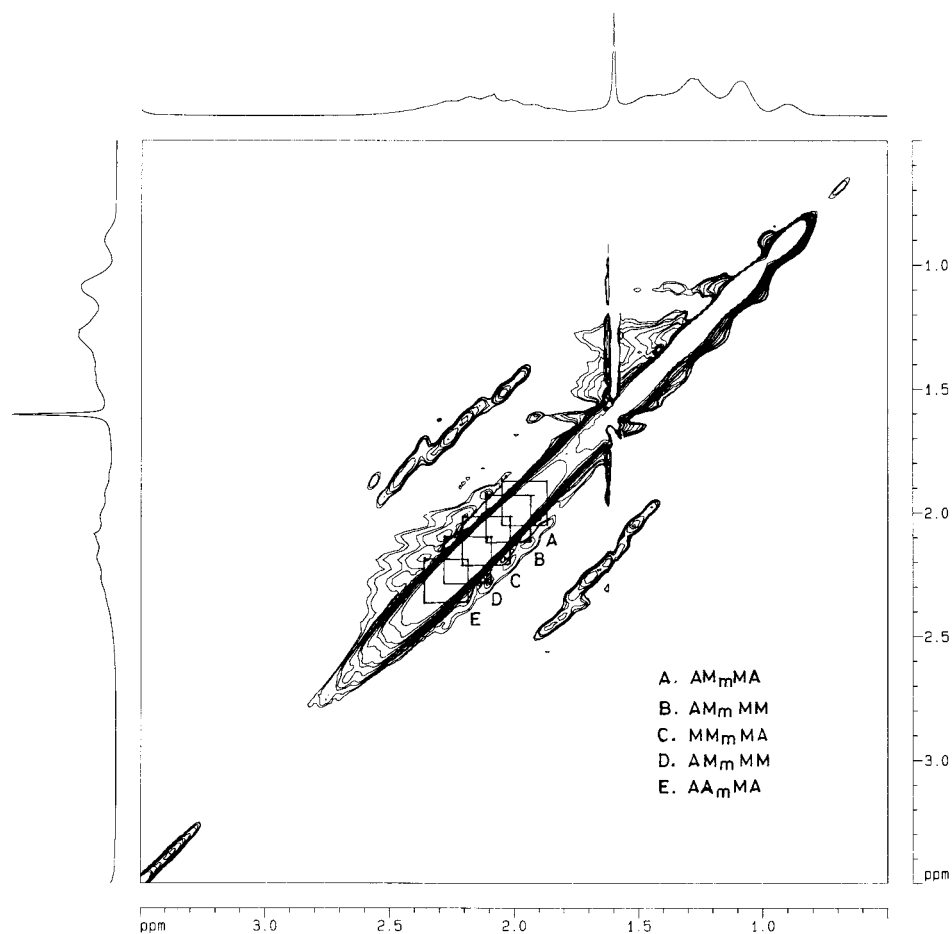


Figure 5 300-MHz ^1H - ^1H 2-D-TOCSY spectra of the A-M copolymer ($F_A = 0.5$) at 4 ms in CDCl_3 .

nary, and methylene carbon resonances of A- and M-monomeric units were in the ranges of δ 16.9–21.6, 45.0–45.71, and 51.96–54.41 ppm, respectively. The methyl and carbonyl carbon resonances were around δ 16.9–21.6 and 173.75–178.75 ppm, respectively. Both these carbon signals show multiplets, indicating sensitivity toward compositional sequences. Thus these signals have been used for the assessment of polymerization mechanism.

Figure 3 shows the expanded methyl carbon resonance signals of A-M copolymers of different compositions. The resonance signals ranges of δ 16.0–18.45 ppm and 18.45–21.0 ppm were assigned to methyl carbon resonance signals of A- and M-monomeric units, respectively. In M-centered triads, there were three envelopes that varied with the change in the copolymer composition and were assigned to the MMM(δ 16.0–17.25 ppm), AMM (δ 17.25–17.75 ppm), and AMA(δ 17.75–18.5 ppm) triad sequences. Therefore these triad fractions show compositional sensitivity. Similarly, in A-centered triads there were three

envelopes that varied with the change in copolymer compositions and were assigned to the MAM(δ 18.5–18.93 ppm), AAM(δ 18.93–19.5 ppm), and AAA(δ 19.5–21.0 ppm) triad sequences. The methyl carbon resonances of AAA triad show further splitting due to compositional sensitivity. The corresponding methyl protons were assigned to the AAAAA (δ 19.75), AAAAM (δ 20.0), and MAAAM (δ 20.5) pentad sequences, respectively, with the help of 2-D HSQC experiments. All these assignments are shown in Figure 4(a–c). The M-centered triad fraction of the methyl carbon resonance show that the cross peaks at δ 16.75/0.92, 17.5/1.11, and 18.0/1.3 ppm were assigned to MMM, AMM, and AMA triads [Fig. 4(a)], respectively. In the A-centered triad fraction, the cross peaks at δ 18.75/1.5, 19.0/1.09, and 19.4/1.24 ppm were assigned to MAM, AAM, and AAA triads, respectively. The methyl carbon signals of the AAA triad show that further splitting was assigned to pentad sequences. Thus the cross peaks at δ 19.75/1.33, 20.0/1.45, and 20.5/1.56 ppm were

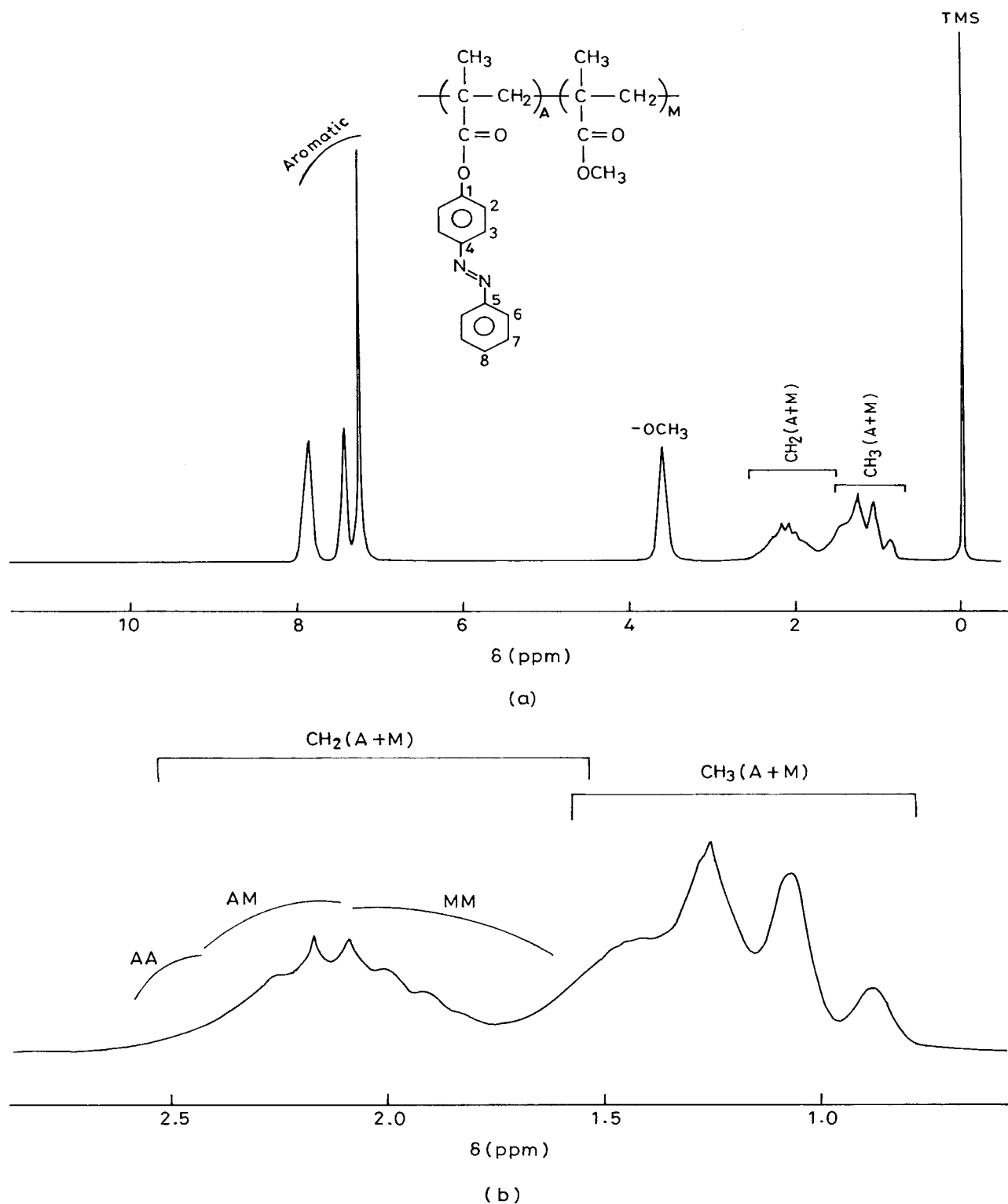


Figure 6 (a)300-MHz $^1\text{H-NMR}$ spectrum of A-M copolymer ($F_A = 0.5$) in CDCl_3 . (b)Expanded methylene and methyl proton resonance signals of A- and M-units

assigned to AAAAA, AAAAM, and MAAAM pentads [Fig.4(b)], respectively. The methylene carbon signals were assigned to three dyad regions—

MM(δ 1.93–2.2 ppm), AM(MA) (δ 2.1–2.35 ppm), and AA(δ 2.35–2.55 ppm)—on the basis of the variation of the signals with the copolymer com-

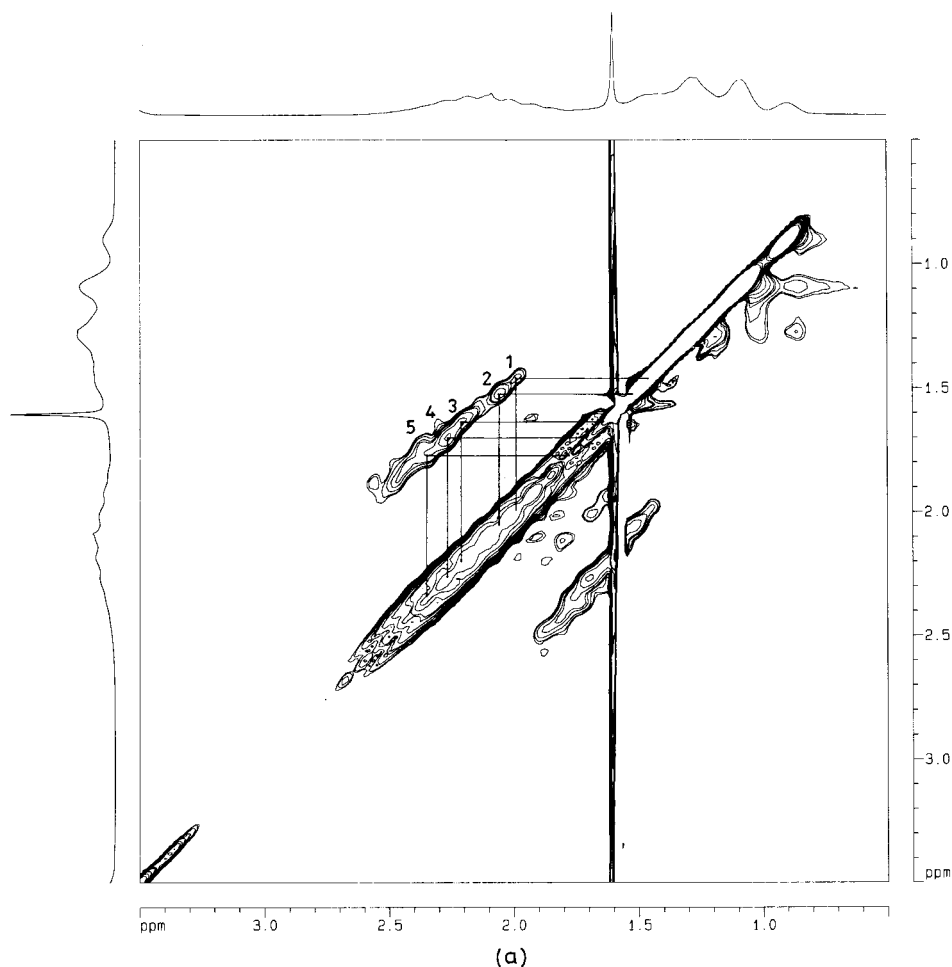


Figure 7 300-MHz ^1H -NMR 2-D-TOCSY spectrum of A-M copolymer: (a) $F_A = 0.5$ (b) $F_A = 0.3$ in CDCl_3 .

position. The further splitting within these dyads, which changed in intensity with the copolymer composition, was assigned to tetrad sequences.

The central methylene protons of all the MM-centered tetrads are nonequivalent and show that two cross peaks in the proton axis [Fig.4(a)] at δ 52.0/2.1 (δ 52.0/1.95), δ 53.7/2.02 (δ 53.7/2.2), and δ 54.25/2.03 (δ 54.25/1.88) ppm are assigned to the AM_mMM , MM_mMA , and AM_mMA meso tetrad sequences, respectively. The central methylene protons of the MMMM tetrad are equivalent and show one cross peak in the proton axis; thus the cross peaks at δ 54.5/1.75 ppm can be assigned to the MM_rMM racemic tetrad sequence. In the AM dyad region, the central methylene protons of AM-centered tetrads are nonequivalent and show that two cross peaks in the proton axis [Fig.4(b)] at δ 52.7/2.28 (δ 52.7/2.1) and δ 54.0/2.37 (δ 54.0/2.2) ppm are assigned to the AA_mMM and AA_mMA meso tetrad sequences, respectively. The AA dyad shows three cross peaks [Fig.4(c)] at δ 53.6/2.45, δ 54.5/2.5, and δ 55.0/2.56 ppm can be assigned to the MAAM,

MAAA, and AAAA tetrad sequences, respectively. All the AM_mMA , AM_mMM , MM_mMA , AA_mMM , and AA_mMA meso tetrads were confirmed by a 2-D TOCSY (4 ms) spectrum at a shorter mixing time and were labeled as A, B, C, D, and E, respectively in Figure 5.

The cross peak at δ 52.2/3.62 ppm was assigned to the methoxy carbon resonance signal. The assignments for methyl and methylene carbon resonance signals obtained from 2-D HSQC experiments are summarized in Table II. With the help of 2-D HSQC spectrum, the ^1H -NMR spectrum of A-M copolymers was assigned and is shown in Figure 6(a,b).

Figure 7(a,b) shows 2-D TOCSY spectra at a higher mixing time (80 ms). The methylene protons of MM dyad shows that two cross peaks at δ 2.0/1.48 and 2.07/1.54 ppm were assigned to the AMMM and AMMA tetrad sequences, respectively. The methylene protons of AM dyad show that three cross peaks at δ 2.21/1.65, δ 2.28/1.71, and 2.35/1.78 ppm were assigned to the MAMM,

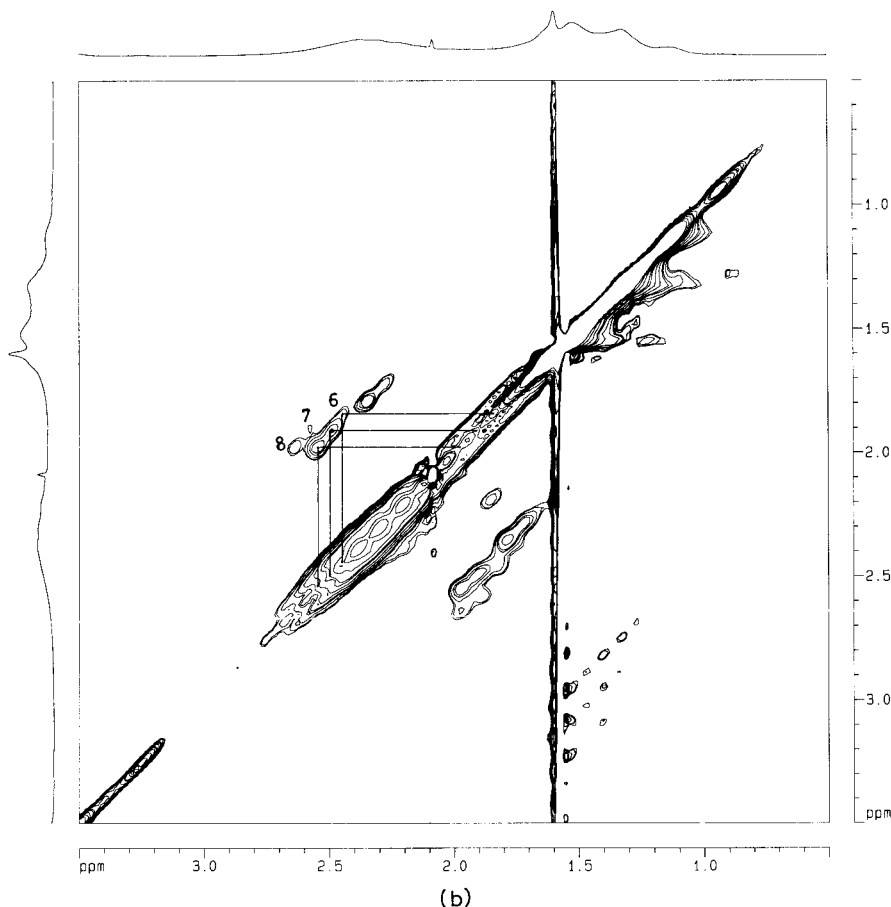


Figure 7 (Continued from the previous page)

AAMM, and AAMA tetrad sequences, respectively. Similarly, the methylene protons of the AA dyad show that three cross peaks at δ 2.45/1.88, δ 2.5/1.94, and 2.55/2.0 ppm were assigned to the AAAA, AAAM, and MAAM tetrad sequences, respectively. All the geminal couplings between the nonequivalent methylene protons in AA, AM, and MM dyads are summarized in Table III.

The expanded carbonyl carbon resonance signals of the A- and M-monomeric units in the A-M copolymer is shown in Figure 8. Since the carbonyl carbon signals in poly(methyl methacrylate) are sensitive to tacticity, the carbonyl carbon signals of A-M copolymer are around δ 176.40–178.75 ppm, which exhibit compositional sensitivity and are assigned to carbonyl carbon signals of M-monomeric unit. The resonance signals around δ 176.38–176.85 ppm decrease, while the resonance signals around δ 177.58–178.75 ppm increase in intensity with the decrease in the concentration of the M unit in the copolymer; therefore the signals around δ 176.38–176.85 and δ 177.58–178.75 ppm were assigned to the MMM and AMA triad se-

quences, respectively. The signals around δ 176.85–177.58 ppm were assigned to the AMM(MMA) triad sequence. The relative fractions of the various triads MMM, MMA and AMA were obtained from the resonance signals' area measurements.

By comparison with poly(*trans*-4 methacryloyloxyazo benzene) (PAB), the signals in the region of δ 173.75–176.2 ppm exhibit compositional sensitivity and are assigned to carbonyl carbon signals of the A-monomeric unit. The resonance signals around δ 175.46–176.2 ppm increases in intensity with an increase in the concentration of the A-unit in the copolymer and are assigned to the AAA triad sequences. The signals in the region of δ 173.75–174.52 ppm, which decrease in intensity with a decrease in the concentration of the M-monomeric unit in the copolymer, were assigned to the MAM triad sequences. The signals in the region of δ 174.52–175.46 ppm were assigned to the AAM (MAA) triad sequence. The relative fractions of AAA, AAM (MAA), and MAM triads were obtained by measuring the area of the

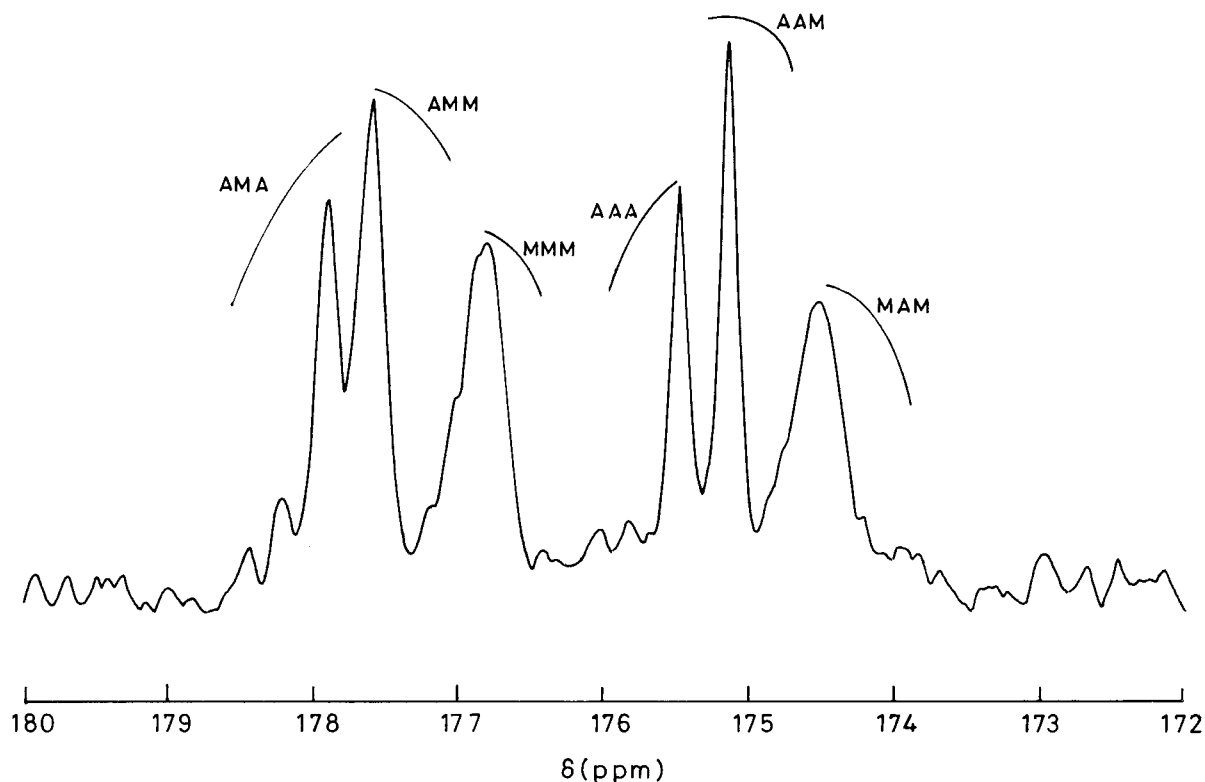


Figure 8 Expanded carbonyl carbon resonance signals of A- and M-monomeric units of the $^{13}\text{C}(^1\text{H})$ -NMR spectra in the A-M copolymer.

resonance signal, using nonlinear least square curve-fitting deconvoluting program.

Assuming the Alfrey-Mayo model to be valid for low-conversion copolymers, the various A- and M-centered triad fractions were calculated using the terminal model reactivity ratios ($r_A = 1.13 \pm 0.10$ and $r_M = 0.50 \pm 0.04$). The relative fraction of A- and M-centered triads determined from the carbonyl carbon signals were in good agreement with those obtained from Harwood's program using the terminal model reactivity ratios shown in Table IV.

CONCLUSION

The reactivity ratios of the A-M copolymer system are $r_A = 1.13 \pm 0.10$ and $r_M = 0.50 \pm 0.04$ (EVM). The overlapping and broad signals in the carbon and proton spectra were assigned completely to various compositional and configurational sequences with the help of 2-D HSQC and TOCSY experiments. The methyl carbon resonances were assigned to pentad sequences, and the methylene carbon resonances were assigned to tetrad sequences with the help of 2-D HSQC experiments. The copolymerization mechanism of

the A-M copolymers were found to follow the first-order Markov model.

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