Microstructure Analysis of Methyl Acrylate/Methyl Methacrylate Copolymers by Two-Dimensional NMR Spectroscopy

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ABSTRACT: Methyl acrylate (A)/methyl methacrylate (B) copolymers of different compositions were synthesized in bulk at 50°C and the compositions were determined from ^{1}H NMR spectra. Reactivity ratios were optimized using the least square methodology. Compositional and configurational assignments were done using two-dimensional (2D) Heteronuclear Single Quantum Correlation (HSQC) and Total Correlation Spectroscopy (TOCSY) experiments. Methylene proton and carbon resonances were assigned for compositional and configurational sensitivity at tetrad level. Carbon resonances of methine group of methyl acrylate were assigned for compositional sensitivity up to triad level with the help of 2D HSQC spectra. α-Methyl group of methyl methacrylate was assigned up to triad level of compositional and configurational placements for carbon and proton resonances by 2D HSQC spectroscopy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1437–1445, 2006

Key words: copolymerization; reactivity ratios; calculations; microstructure; NMR

INTRODUCTION

NMR is the most widely used technique for the qualitative and quantitative analysis of chain microstructure and polymer composition determination.[1,2] Two-dimensional (2D) NMR has been widely accepted and practiced in a large spectrum of polymer studies, especially for solving complex chemical structures of polymers involving main chain structure elucidation (regioisomerism, stereochemical configuration, geometrical isomerism, branching and crosslinking) and identification of chain ends.[3–14]

Homo- and copolymers of acrylates and methacrylates exhibit large number of physical properties, which make them important from commercial viewpoint, inducing many groups to study their microstructure.[15–28] Kim and Harwood have reported the sequence distribution of α-methyl, methane, and methylene carbon resonances in methyl acrylate/methyl methacrylate copolymers by ^{13}C{^{1}H} NMR spectroscopy.[18] Brar et al. have reported the analysis of α-methyl, methine, methylene, and carbonyl carbon resonances by ^{13}C{^{1}H} NMR and 2D Heteronuclear Single Quantum Correlation (HSQC) NMR spectra of ethyl acrylate/methyl methacrylate copolymers.[19]

Nguyen et al. and Matlengiewicz et al. have done exhaustive study on carbonyl and methylene carbon assignments of ethyl acrylate/methyl methacrylate copolymers based on chemical shift parameterization and spectral simulation.[20,21]

To the best of our knowledge, the 2D NMR spectral analysis of methyl acrylate/methyl methacrylate copolymers has not been reported earlier. With the aim of investigating the sequence analysis of methyl acrylate (A)/methyl methacrylate (B) copolymer system to a high level, 2D HSQC and 2D Total Correlation Spectroscopy (TOCSY) spectra of copolymers were analyzed. Results show the importance of assignments based on 2D NMR spectroscopy, especially for methylene carbon, and assignment of ^{1}H NMR spectrum, which otherwise were very difficult to make explicitly. Using the assigned ^{1}H NMR spectra, composition of the copolymers was determined. The reactivity ratios have been calculated using the least square methodology, incorporating self consistency approach for the determination of error weights.[29–31] The optimized reactivity ratios have been compared with those obtained from the nonlinear least square error-in-variable (RREVM) method.[32]

EXPERIMENTAL

Copolymer synthesis

Methyl acrylate (Merck) and methyl methacrylate (Merck) were distilled under reduced pressure and stored at low temperature. AIBN (Fluka), the free
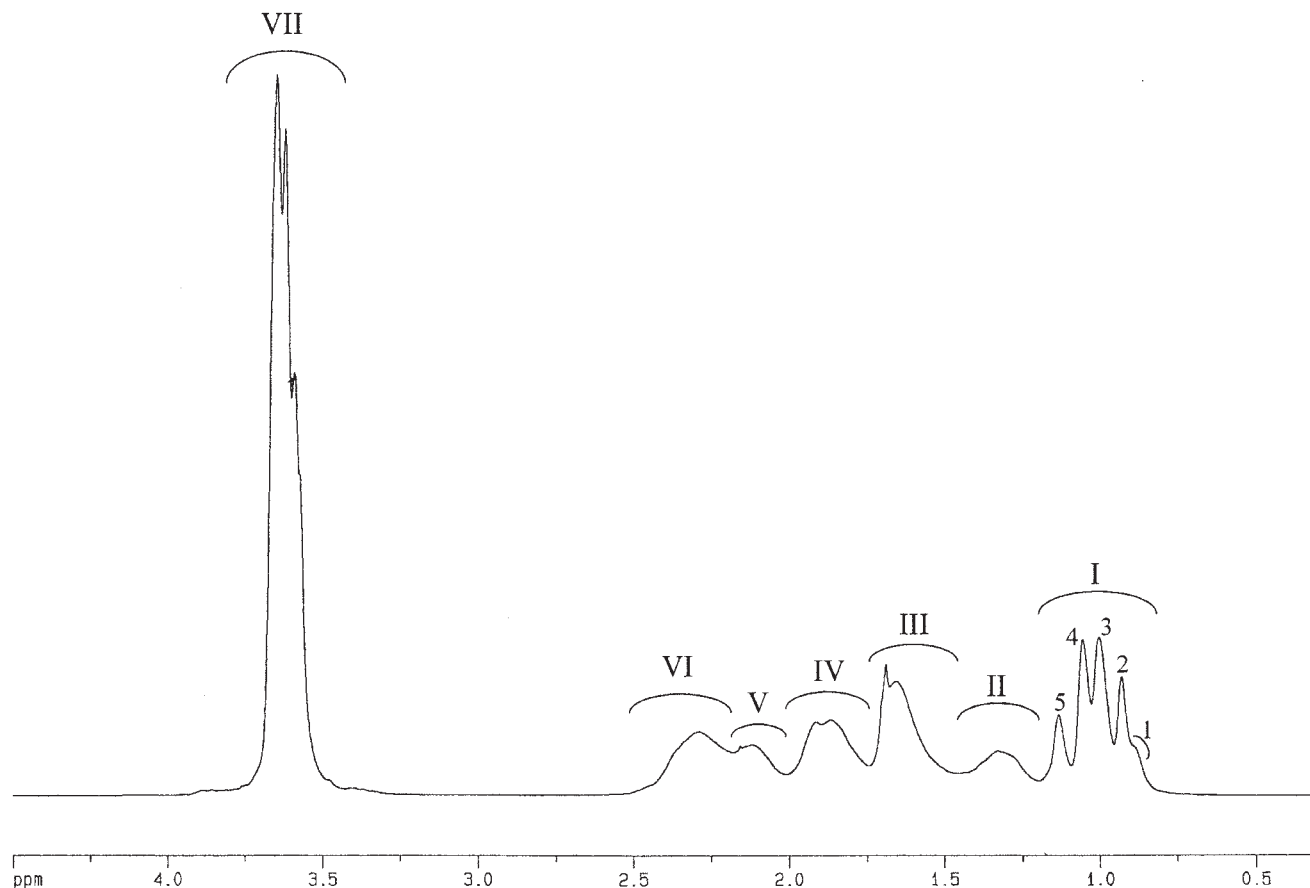

Figure 1   300 MHz ^{1}H spectrum of the methyl acrylate (A)/methyl methacrylate (B) copolymer of composition ($F_A = 0.579$ in CDCl$_3$ at 45°C).

radical initiator was recrystallized from distilled methanol, and dried and stored at low temperature.

Poly(methyl acrylate), poly(methyl methacrylate), and a series of methyl acrylate (A)/methyl methacrylate (B) copolymers were synthesized in bulk at 50°C using AIBN (0.05 mol %) as initiator. The polymerization was stopped at low conversion by precipitating the reaction mixtures in large excess of methanol–water mixture, to prevent composition drift. Further purification was done using chloroform/methanol–water mixture as solvent/precipitant system. Polymers were then dried in vacuum and conversion was determined gravimetrically.

NMR studies

The one-dimensional (1D) and two-dimensional (2D) NMR spectra were recorded on Bruker DPX-300 spectrometer in CDCl$_3$ at frequencies of 300.13 and 75.5 MHz for ^{1}H and ^{13}C, respectively, at 45°C. ^{1}H NMR spectra were recorded with 10 s delay time. The details of the experiments are given in our earlier publication.[24]

Reactivity ratios determination

Reactivity ratios were determined from the copolymer composition using the least square methodology adopted in Genetic Algorithm. The genetic algorithm provided the advantage over traditional search algorithms of it, being capable of searching through very large space. The least square methodology for the optimization of the reactivity ratios is based on the principle of minimizing the sum of weighted residuals:

TABLE I
Infeed and Outfeed Mole Fraction of Methyl Acrylate (A) and Weight % Conversion in Methyl Acrylate (A)/ Methyl Methacrylate (B) Copolymerization

f_A	F_A	Conversion (wt %)
0.90	0.76	4.7
0.86	0.66	4.1
0.80	0.58	2.6
0.60	0.37	3.1
0.30	0.12	3.7
0.20	0.09	2.2

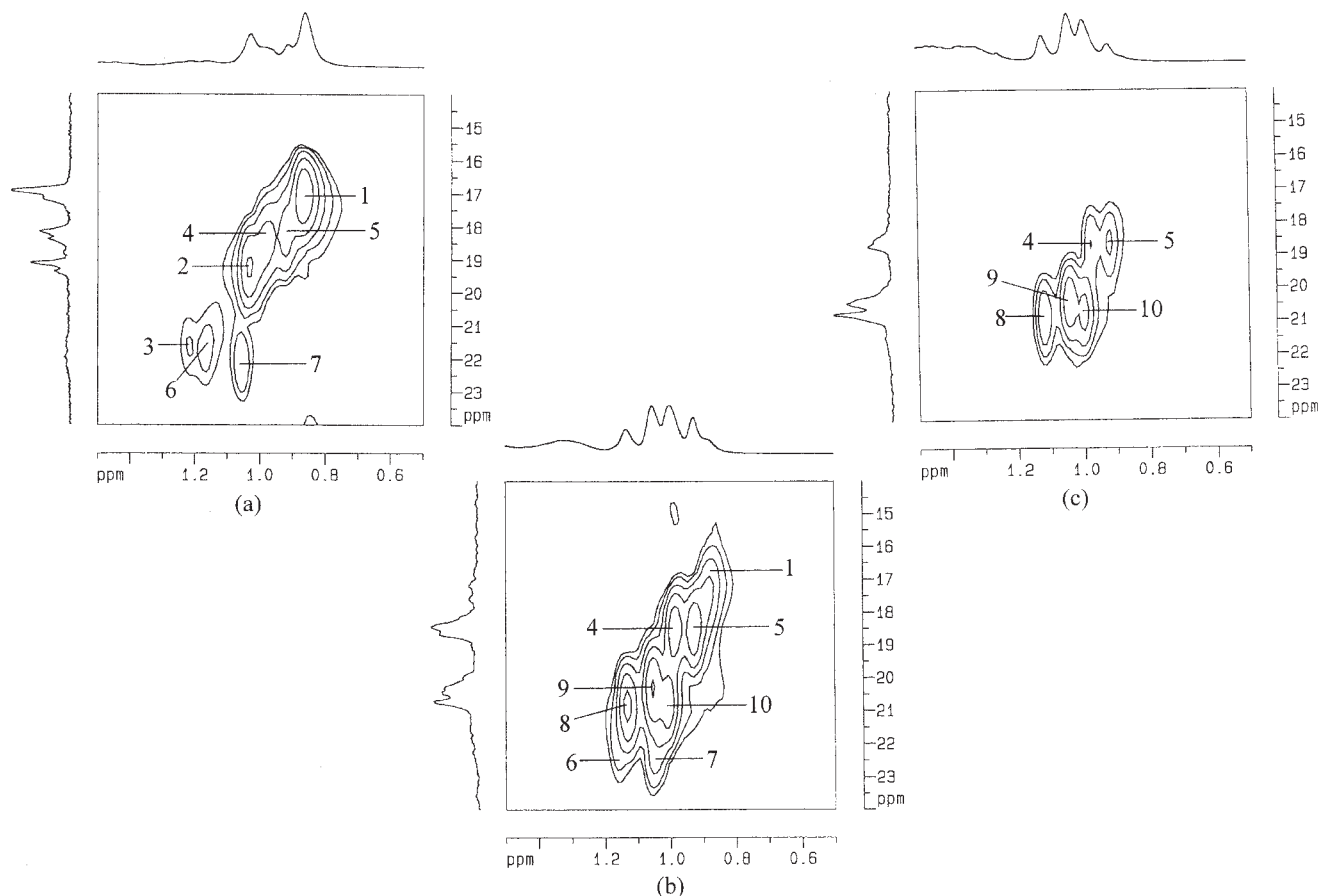**Figure 2** α-Methyl region in 2D HSQC NMR spectra of the methyl acrylate (A)/methyl methacrylate (B) copolymer in CDCl$_3$ at 45°C (F_A = 0.092 (a), 0.579 (b), and 0.761 (c)).

RESULTS AND DISCUSSION

Kim and Harwood have assigned α-methyl, methylene, and methine carbon resonances up to triad and tetrad level of configurational sensitivity.[18] They have made assignments based on the change in intensities of various resonance signals with copolymer compo-

$$ss(r_1,r_2) = \sum_{i=1}^{n}\{w_i[y_i - f(x_i,r_1,r_2)]^2\}$$

where, r_1 and r_2 are the reactivity ratios, w_i is the weighting factor included to take account of the error involved in the measurements of outfeed compositions, y_i is the experimental outfeed composition, and x_i is the infeed. $f(x_i, r_1, r_2)$ is the function of infeed and reactivity ratios, giving the value of theoretical outfeed composition.[29–31]

The weighting factor w_i is the reciprocal variance, $w_i = 1/\sigma_i$. When the error is unknown the assumption of constant relative error can be assumed. To begin, $w_i = 1$ is assumed then r_1 and r_2 are optimized. The values of these r_1 and r_2 are then used to calculate the theoretical response i.e., r_1 and r_2 are substituted as r_1' and r_2', respectively, in the weighting factor ($w_i = 1/\sigma_i \approx 1/f(x_i, r_1', r_2')^2$) and r_1 and r_2 are optimized again. This iteration is continued till r_1 and r_2 converged and returned the same values of reactivity ratios as used in weighting factor i.e., optimized in the previous optimization.

TABLE II
Assignments of the α-CH$_3$ Carbon Resonances of Methyl Acrylate (A)/Methyl Methacrylate (B) Copolymers from 2D HSQC Spectra

Cross-peak no.	Cross-peak assignment	Cross-peak position (ppm)
1	BrBrB	16.9/0.8
2	BrBmB	19.1/1.02
3	BmBmB	21.5/1.20
4	ABrB	18.4/0.92
5	ABrB	18.4/1.00
6	ABmB	21.5/1.17
7	ABmB	22.1/1.05
8	ABA	20.7/1.13
9	ABA	20.3/1.05
10	ABA	20.5/1.00

TABLE III
Assignments of ^{1}H Spectrum of Methyl Acrylate (A)/Methyl Methacrylate (B) Copolymers

Resonance region	Assignment
I (0.70–1.20 ppm)	α-CH$_3$
II (1.20–1.46 ppm)	CH$_2$ of AmB (Hb), AmA (Hb), and BrBmBrB (Hb)
III (1.46–1.74 ppm)	CH$_2$ of ArA and ArB (Hb)
IV (1.74–2.00 ppm)	CH$_2$ of BmBrBrB, BrBmBrB, BrBrBrB, ABBA, ABBB, AmA (Ha), and ArB (Ha)
V (2.00–2.17 ppm)	CH$_2$ of AmB (Ha)
VI (2.17–2.50 ppm)	CH
VII (3.3–3.9 ppm)	OCH$_{3(A + B)}$
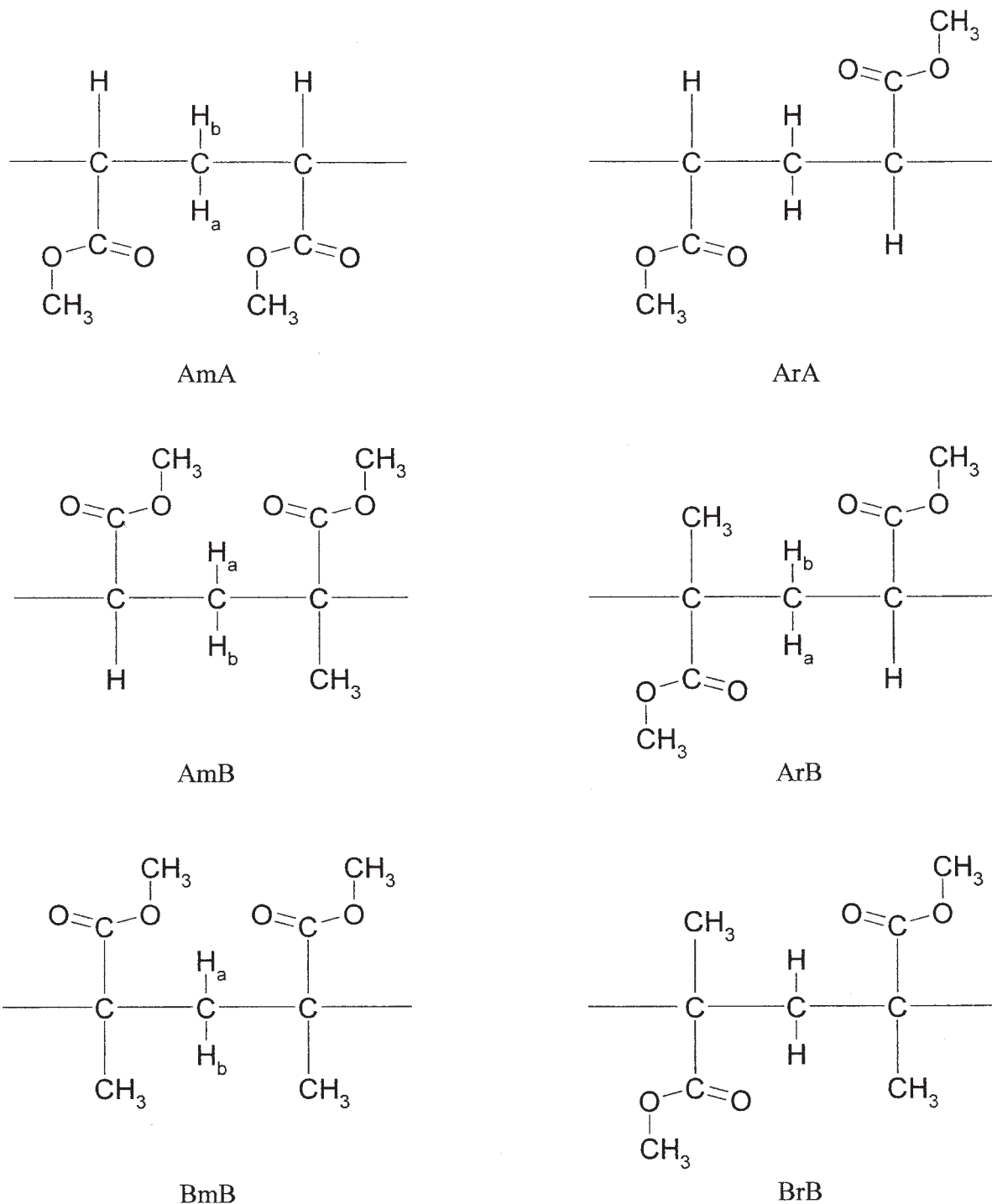
Scheme 1 Structures of the AA, AB, and BB dyads showing the presence of methylene protons in different environments.

(a)

(b)

(c)
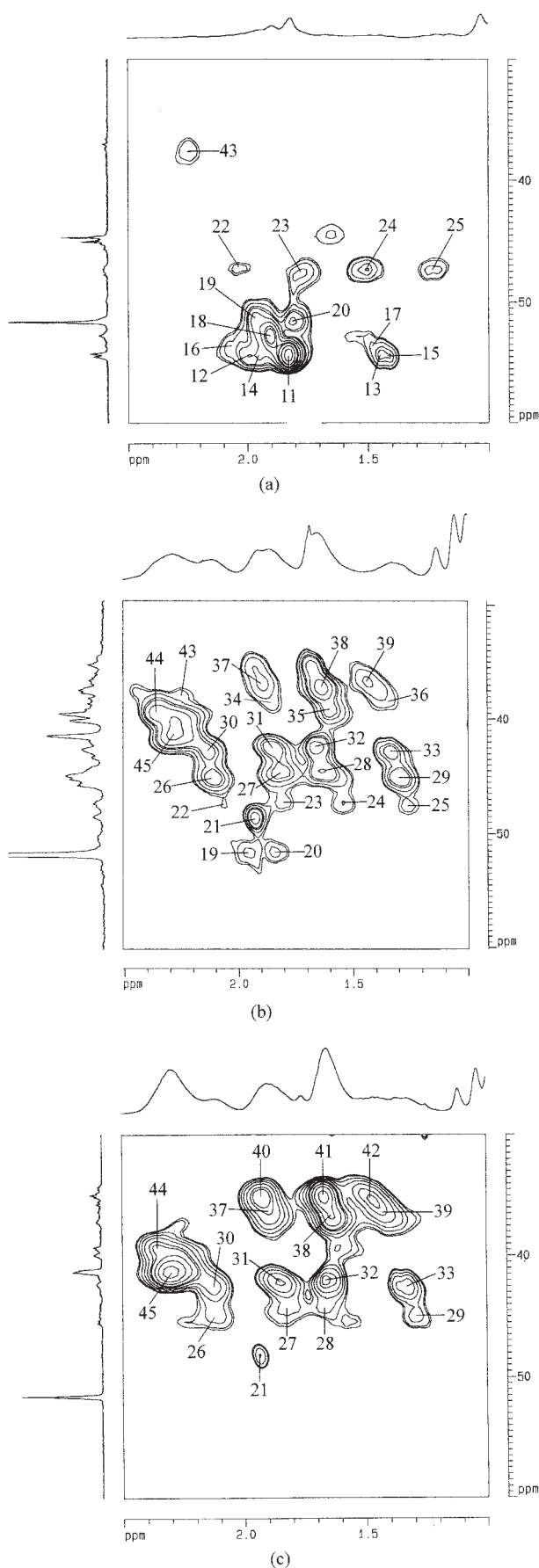
sition and then comparing the change in intensities with that of the calculated signal intensities using the computer program developed by Harwood.[33] This work, incorporating 2D HSQC and 2D TOCSY experiments, augments the 1D ^{13}C{^{1}H} NMR assignments done by Harwood.. Variations in the intensities of cross-peaks in 2D HSQC and 2D TOCSY spectra with change in composition was analyzed and assignments were done. 1D ^{13}C{^{1}H} NMR assignments made by Kim and Harwood[18] and assignments of the 2D HSQC spectra of homopolymers[22,24] were used for sequence analysis.

Copolymer composition and reactivity ratios determination

Figure 1 shows the ^{1}H NMR spectrum of methyl acrylate (A)/methyl methacrylate (B) copolymer ($F_A = 0.579$). Using 2D HSQC spectra, it was ascertained that ^{1}H NMR signal of α-methyl of methyl methacrylate extends from 0.75 to 1.20 ppm, region I in Figure 1. The combined signal of $OCH_{3(A + B)}$ protons is segregated from rest of the signals and is centered on 3.6 ppm, region VII in Figure 1. The copolymer composition was calculated from the intensities of methoxy and α-methyl protons by using the following equation:

$$F_A = 1 - \frac{I(\alpha - \text{methyl})_B}{I(\text{OCH}_3)_{A+B}}$$

where $I(\alpha\text{-methyl})_B$ is the area under the α-methyl resonance signals of B unit and $I(\text{OCH}_3)_{A + B}$ is the area under the methoxy protons resonance signals for both A and B units.

The data of methyl acrylate/methyl methacrylate copolymerization is given in Table I. the reactivity ratios, calculated using the above explained least square methodology, were $r_A = 0.32$ and $r_B = 2.63$. Monomer reactivity ratios for the methyl acrylate (A) and methyl methacrylate (B) copolymers calculated using nonlinear error-in-variables method with the RREVM computer program were $r_A = 0.32$ and $r_B = 2.61$.[32] The reactivity ratios calculated from both the methods were in good agreement.

α-Methyl carbon and proton resonances

α-Methyl group of methyl methacrylate is sensitive to both the conformational and configurational place-

Figure 3 2D HSQC NMR spectra of the methyl acrylate (A)/methyl methacrylate (B) copolymers in CDCl$_3$ at 45°C ($F_A = 0.092$ (a), 0.579 (b), and 0.761 (c)), showing methylene and methine region.

TABLE IV
Assignments of the Methylene Carbon Resonances of Methyl Acrylate (A)/Methyl Methacrylate (B) Copolymers

Cross-peak no.	Cross-peak assignment	Cross-peak position (ppm)
11	BrBrBrB	54.4/1.81
12	BmBrBmBrBrB (Ha)	54.5/1.99
13	BmBrBmBrBrB (Hb)	54.5/1.44
14	BrBrBmBrBrB (Ha)	54.5/1.95
15	BrBrBmBrBrB (Hb)	54.5/1.41
16	BmBmBrB (Ha)	53.6/2.07
17	BmBmBrB (Hb)	53.6/1.47
18	BmBrBrB	53.0/1.89
19	ABBB	51.5/1.95
20	ABBB	51.5/1.84
21	ABBA	48.4/1.92
22	BAmBB (Ha)	47.3/2.04
23	BArBB (Ha)	47.0/1.77
24	BArBB (Hb)	47.0/1.52
25	BAmBB (Hb)	47.3/1.23
26	AAmBB/BAmBA (Ha)	44.8/2.1
27	AArBB/BArBA (Ha)	44.3/1.82
28	AArBB/BArBA (Hb)	44.3/1.62
29	AAmBB/BAmBA (Hb)	44.8/1.29
30	AAmBA (Ha)	42.6/2.13
31	AArBA (Ha)	42.2/1.84
32	AArBA (Hb)	42.2/1.65
33	AAmBA (Hb)	42.6/1.33
34	BAmAB (Ha)	38.4/1.86
35	BArAB	38.8/1.62
36	BAmAB (Hb)	38.4/1.37
37	AAmAB (Ha)	36.5/1.89
38	AarAB	36.9/1.63
39	AAmAB (Hb)	36.4/1.43
40	AAmAA (Ha)	35.3/1.93
41	AarAA	35.1/1.67
42	AAmAA (Hb)	35.3/1.46

ments. It has got a spread of about 6.2 ppm on carbon axis in the methyl acrylate/methyl methacrylate copolymer, and its carbon resonances were divided into five regions, as reported by Kim and Harwood.[18]

2D HSQC spectra revealed the five regions of carbon resonances, as shown in Figure 2. The 2D HSQC assignments of the α-methyl group are listed in the Table II. On the basis of the variation of intensities of cross-peaks as a function of copolymer composition, the assignments of 2D HSQC spectra were made. The cross-peak 1 was assigned to BrBrB triad. BrBmB and BmBmB triads were assigned to the cross-peaks 2 and 3, respectively. The cross-peaks 4 and 5 were assigned to BrBA triads. The BmBA triad, which was very difficult to observe in the 1D ^{13}C{^{1}H} spectra, gave cross-peaks 6 and 7, which could be easily identified as shown in Figure 2(a). Cross-peaks 8, 9, and 10 were assigned to ABA triad.^{1}H NMR resonances of α-methyl were split into five major regions, labeled from 1 to 5, as shown in region I in the Figure 1, the assignments are given in Table III.

Methylene carbon and proton resonances

Methylene carbon resonances are spread over 22 ppm range (33.5–55.5 ppm), and because of its symmetry is sensitive to dyad, tetrad and higher compositional and configurational placements. Matlengiewicz *et al.* have made complete conformational and configurational assignments of methylene carbon of ethyl acrylate/methyl methacrylate copolymers upto tetrad level, based on chemical shift parameterization and spectral simulation.[21]

Methylene subspectra, obtained by subtracting DEPT-135 spectra from DEPT-45 spectra, were analyzed for 1D NMR analysis of resonance signals of methylene group. 2D TOCSY spectra were used to confirm the 1,2 bond geminal couplings between nonequivalent protons of the same methylene group. Methylene proton resonance signals, which were overlapped and couldn't be assigned by ^{1}H NMR spectral analysis only, were assigned from one-to-one correlation between carbon and proton signals in the 2D HSQC spectra.

The protons in the racemic methylene of BrB and ArA centered tetrads are in same environment as depicted in Scheme 1, resulting in a single cross-peak in the 2D HSQC spectra. The two nonequivalent methylene meso protons, Ha and Hb, of AA and BB centered tetrads (Scheme 1) result in two cross-peaks in the 2D HSQC spectra and a cross-correlation peak in 2D TOCSY spectra (Ha proton was attributed to the proton having high chemical shift and Hb having lower chemical shift). Thus, 2D TOCSY spectra enabled to differentiate between the meso and racemic protons and confirm the 2D HSQC assignments.

2D HSQC spectra are given in the Figure 3 and the assignments are listed in Table IV. Based on the assignments of PMMA, configurational assignments of BBBB tetrads shown in Figure 3(a) were done. BrBrBrB (Ha) was assigned to the cross-peak 11. BmBrBmBrBrB (Ha) and BrBrBmBrBrB (Ha) tetrads were attributed to the cross-peaks 12 and 14 and; BmBrBmBrBrB (Hb) and BrBrBmBrBrB (Hb) to the cross-peaks 13 and 15. 2D TOCSY spectra are given in Figure 4 and the assignments of cross-correlation peaks are given in Table V. Ha and Hb protons of BrBmBrB tetrads, being nonequivalent, resulted in cross-correlation peak 1′ in the 2D TOCSY spectrum (Fig. 4(a)). Cross-peaks 16 and 17 were assigned to the BmBmBrB (Ha) and BmBmBrB (Hb) tetrads, respectively. Ha and Hb protons coupled to give cross-correlation peak 2′ in TOCSY spectrum (Fig. 4(a)). BmBrBrB was assigned to the cross-peak 18.

ABBB and ABBA tetrads of copolymer were assigned on observing the change in intensities of the cross-peaks with change in composition. ABBB gave rise to two cross-peaks 19 and 20 which are present in Figure 3 (a) and (b). ABBA tetrad, having more A

(a)

(b)

(c)
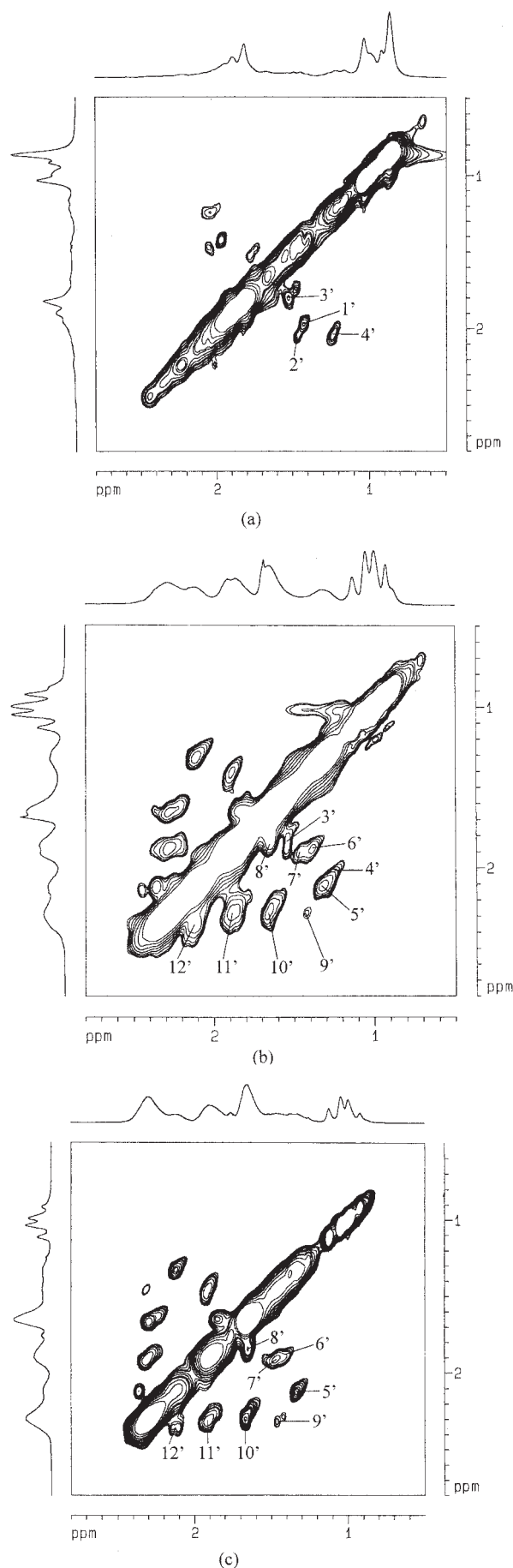
monomer content than ABBB tetrad, has one corresponding cross-peak 21 and can be observed both in Figures 3(b) and 3(c) i.e., at higher F_A also, thus enabling to differentiate between ABBB and ABBA.

The methylene protons Ha and Hb of both the AmB and ArB centered tetrads are in different magnetic environment as shown in Scheme 1, and thus they result in two cross-peaks by coupling with the methylene carbon in the 2D HSQC spectra. Ha and Hb of AmB and ArB, being nonequivalent, also give cross-correlation peaks in the 2D TOCSY spectra, enabling to differentiate between cross-peaks of AmB and ArB in the 2D HSQC spectra. BABB tetrad concentration decreases with increase in F_A, and on this basis BABB tetrad was assigned. BAmBB (Ha) and BAmBB (Hb) tetrads were assigned to the cross-peaks 22 and 25 respectively, as marked in Figures 3(a) and 3(b), these nonequivalent protons have cross-correlation peak 4′ in 2D TOCSY. BArBB (Ha) and BArBB (Hb) were assigned to the cross-peaks 23 and 24, respectively. Ha and Hb of BArBB tetrad give cross-correlation peak 3′ in 2D TOCSY (Figs. 4(a) and 4(b)).

AAmBB/BAmBA (Ha), AAmBB/BAmBA (Hb), AArBB/BArBA (Ha), and AArBB/BArBA (Hb) were attributed to the cross-peaks 26, 29, 27 and 28, respectively. AAmBA (Ha), AAmBA (Hb), AArBA (Ha), and AArBA (Hb) were assigned to the cross-peaks 30, 33, 31, and 32, respectively. Ha and Hb of AAmBB/BAmBA and AAmBA coupled to give cross-correlation peak 5′ and Ha and Hb of AArBB/BArBA and AArBA due to the geminal coupling gave cross-correlation peak 8′ in 2D TOCSY spectra.

AA dyad centered tetrads showed compositional and conformational sensitivity. BAmAB (Ha), BArAB, and BAmAB (Hb) tetrads have cross-peaks 34, 35, and 36, respectively. AAmAB (Ha), AArAB, and AAmAB (Hb) have cross-peaks 37, 38, and 39, respectively. Methylene protons, Ha and Hb, of BAmAB/AAmAB gave cross-correlation peak 6′ in the 2D TOCSY spectra as shown in Figures 4(b) and 4(c). AAAA tetrad was assigned by comparing with 2D HSQC and 2D TOCSY spectra of poly (methyl acrylate).[22] AAmAA (Ha) was assigned to the cross-peak 40, AAmAA (Hb) to cross-peak 41, and cross-peak 42 was assigned to AArAA tetrad. Geminal coupling between Ha and Hb protons was assigned to the cross-correlation peak 7′.

This work shows the importance of 2D NMR experiments in understanding the microstructure of polymers. A large number of assignments have been made, which are difficult to make on the basis of 1D NMR experiments only. To distinguish between groups

Figure 4 2D TOCSY NMR spectra of the methyl acrylate (A)/methyl methacrylate (B) copolymers in CDCl$_3$ at 45°C (F_A = 0.092 (a), 0.579 (b), and 0.761 (c)).

^{1}H-^{1}H Cross-Correlations between Nonequivalent Geminal Protons of Methylene and between Methine Protons and Methylene Protons in Methyl Acrylate (A)/Methyl Methacrylate (B) Copolymers Observed from the TOCSY Spectra

Cross-correlation peak no.	Coupled protons		Cross-correlation peak position (ppm)
	Proton I	Proton II	
1'	CH$_2$ of BrBmBrB (Ha)	CH$_2$ of BrBmBrB (Hb)	1.95/1.41
2'	CH$_2$ of BmBmBrB (Ha)	CH$_2$ of BmBmBrB (Hb)	2.06/1.47
3'	CH$_2$ of BArBB (Ha)	CH$_2$ of BArBB (Hb)	1.77/1.52
4'	CH$_2$ of BAmBB (Ha)	CH$_2$ of BAmBB (Hb)	2.03/1.23
5'	CH$_2$ of AAmBB/BAmBA/AAmBA (Ha)	CH$_2$ of AAmBB/BAmBA/AAmBA (Hb)	2.13/1.3
6'	CH$_2$ of BAmAB/AAmAB (Ha)	CH$_2$ of BAmAB/AAmAB (Hb)	1.88/1.35
7'	CH$_2$ of AAmAA (Ha)	CH$_2$ of AAmAA (Hb)	1.89/1.44
8'	CH$_2$ of AArBB/BArBA/AArBA (Ha)	CH$_2$ of AArBB/BArBA/AArBA (Hb)	1.84/1.64
9'	CH of A	CH$_2$ of AmA (Hb)/AmB (Hb)	2.2/1.4
10'	CH of A	CH$_2$ of ArA/ArB (Hb)	2.2/1.6
11'	CH of A	CH$_2$ of AmA (Ha)/ArB (Ha)	2.2/1.8
12'	CH of A	CH$_2$ of AmB (Ha)	2.3/2.1

such as AmB and ArB, 2D HSQC supported by 2D TOCSY experiments proves to be a very powerful and reliable technique. There is good agreement of assignments made using 2D NMR experiments and those reported by Kim and Harwood[18] and Matlengiewicz et al.[21]

Based on the 2D HSQC assignments, which were further confirmed by 2D TOCSY studies, ^{1}H NMR spectra were assigned. Assigned ^{1}H NMR spectrum of the composition ($F_A = 0.579$) is given in Figure 1. Proton spectra were divided into seven regions. The CH$_2$ protons are occupying II, III, IV, and V regions. Table III is listing the assignments of ^{1}H spectra.

Methine carbon assignments

Methine group of methyl acrylate was assigned upto triad level of compositional sensitivity in the copolymer, based on the 2D HSQC assignments. DEPT-90 spectra were used to distinguish the methine signals for 1D NMR analysis, as they were overlapping with the methylene resonances. 2D TOCSY studies were used to ascertain these assignments by assigning 1,3 bond order couplings between methylene protons and methine protons of A monomer in AA and AB centered methylene. The assignments done agree with those done by Kim and Harwood.[18]

BAB triad was assigned to the cross-peak 43, and BAA and AAA triads to the cross-peaks 44 and 45, respectively, as shown in Figure 3. The chemical shifts of methine group on proton axis were in a very narrow range (2.17–2.50 ppm), thus assignments up to triad level were possible. The cross-correlation peaks 9', 10', 11', and 12', shown in Figure 4, were assigned to the 1,3 bond order couplings of CH with CH$_2$ of AmA (Hb)/AmB (Hb), ArA/ArB (Hb), AmA (Ha)/ArB (Ha), and AmB (Ha), respectively.

The methine protons are spread in the region labeled VI in Figure 1, in the range 2.17–2.50 ppm.

CONCLUSIONS

The reactivity ratios optimized for the methyl acrylate (A)/methyl methacrylate (B) copolymerization from the least square methodology and RREVM program are $r_A = 0.32$, $r_B = 2.63$ and $r_A = 0.32$, $r_B = 2.61$, respectively. The methylene carbon and proton resonances were assigned up to tetrad level of compositional and configurational sensitivity. Methine group of methyl acrylate was assigned upto triad level of compositional sensitivity for carbon resonances based on the 2D HSQC spectral analysis. The assignments were further confirmed using 2D TOCSY experiments. Carbon resonances of α-methyl group were assigned upto triad level of compositional sensitivity. The complexity in 1D NMR spectra precludes the assignments made evidently from the analysis of 2D HSQC and 2D TOCSY spectra. One-to-one correlation between carbon and proton in the 2D HSQC spectra and cross-correlation peaks between nonequivalent protons in the 2D TOCSY experiments enabled to assign the methylene, methane, and α-methyl proton resonance signals in the overlapping ^{1}H NMR spectra unequivocally.

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