

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

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**ABSTRACT:** In the present article, a comprehensive two-dimensional heteronuclear multi bond correlation (HMBC) spectral analysis of methyl acrylate (A)/methyl methacrylate (B) copolymers is reported. The methylene carbon and methine carbon resonances assigned from the 2D HSQC spectroscopy were established by analyzing the two and three bond order couplings with  $\alpha$ -methyl protons, methylene protons, and methine protons. Quaternary carbon resonances of the B unit were assigned by investigating the two bond order couplings with  $\alpha$ -methyl protons and methylene

protons. Assignments of carbonyl carbon resonances based on the analysis of three bond couplings with  $\alpha$ -methyl protons and methylene protons are reported. The analyses present comprehensive assignments of the carbonyl carbon resonances showing the critical contribution of 2D HMBC spectroscopy in the indirect analysis of carbon resonances. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2174–2181, 2006

**Key words:** copolymerization; microstructure; NMR; HMBC

## INTRODUCTION

NMR spectroscopy with the newer experiments and advancement of the instrumentation has become all the more an indispensable tool for a polymer chemist and physicists.<sup>1–3</sup> In the recent years, analysis of long range hetero atom (e.g., carbon)–proton couplings from the gradient HMBC spectral analysis has proven to be highly informative in the microstructure analysis of polymers.<sup>4–11</sup>

Methyl acrylate/methyl methacrylate copolymers being commercial polymers find large range of applications. Detailed understanding of its microstructure thus becomes important to understand its properties better. Kim and Harwood reported the 1D NMR analysis of the methyl acrylate/methyl methacrylate copolymers and discussed  $\alpha$ -methyl, methylene, and methine resonances.<sup>12</sup> Owing to the complexity associated with the carbonyl carbon resonances, they did not reported carbonyl carbon assignments. Roman and Valero<sup>13</sup> and Brar et al.<sup>14</sup> discussed the assignments of the carbonyl carbon of ethyl acrylate/methyl methacrylate copolymers. Matlengiewicz et al. reported exhaustive assignments of carbonyl carbon of ethyl acrylate/methyl methacrylate copolymers based

on the chemical shift parameterization and spectral simulation.<sup>15,16</sup>

The carbonyl carbon assignments based on the experimental analysis of their couplings with methylene protons and  $\alpha$ -methyl protons were done to overcome any speculation for the resonance analysis. Assignments of the quaternary carbon of methyl methacrylate unit have been done from 2D HMBC spectral analysis. Assignments of methylene carbon done on the basis of 2D HSQC and 2D TOCSY spectral analysis were ascertained.<sup>17</sup> In this report, rigorous compositional and configurational assignments of the methyl acrylate/methyl methacrylate copolymers from investigating two and three bond order  $^1\text{H}/^{13}\text{C}$  couplings from HMBC spectrum are reported for the unambiguous microstructure analysis.

## EXPERIMENTAL

### Copolymer synthesis

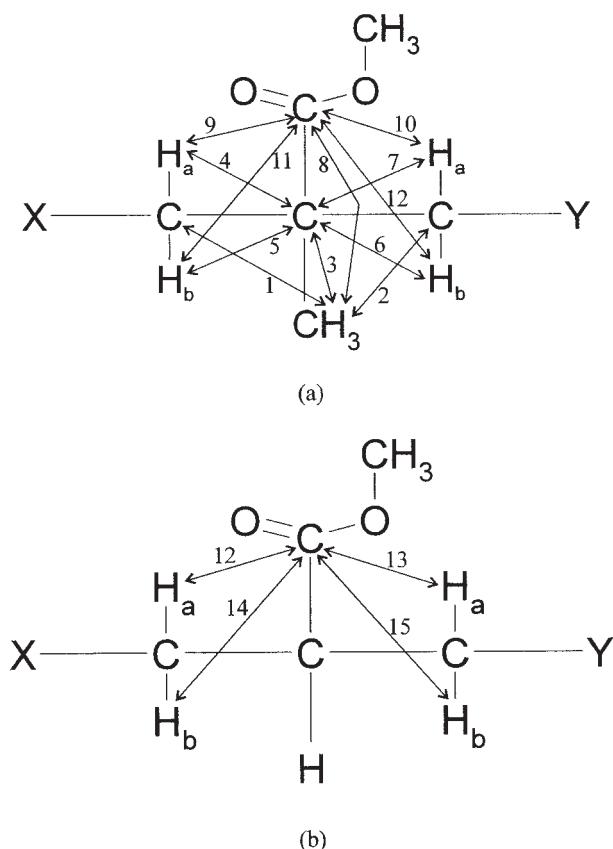
A series of methyl acrylate (A)–methyl methacrylate (B) copolymers were synthesized in bulk at 50°C, using AIBN (0.05 mol %) as initiator. Details of the polymerization are given in earlier publication by Brar et al.<sup>17</sup>

### NMR studies

The 1D and 2D NMR spectra were recorded on Bruker DPX-300 spectrometer in  $\text{CDCl}_3$  at frequencies of 300.13 and 75.5 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively, at

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**Scheme 1.** A and B centered triads showing the couplings analyzed from the 2D HMBC spectral analysis of methyl acrylate/methyl methacrylate copolymers.

45°C. The details of the experiments are given in our earlier publication.<sup>18</sup>

## RESULTS AND DISCUSSION

2D HMBC spectral analysis of the methyl acrylate (A)/methyl methacrylate (B) copolymers has been discussed to cross-examine the assignments from the 2D HSQC and 2D TOCSY spectral analysis. Roman and Valero<sup>13</sup> and Brar et al.<sup>14</sup> reported the carbonyl carbon assignments of ethyl acrylate/methyl methacrylate copolymers, based on the quantitative evaluation of resonances at triad level of compositional and configurational assignments. Matlengiewicz et al. reported the assignments of carbonyl carbon resonances based on the empirical chemical shift rules and spectral simulation for ethyl acrylate/methyl methacrylate copolymers.<sup>15,16</sup> The direct experimental confirmation based on the analysis of the couplings of carbonyl carbon with methylene protons and  $\alpha$ -methyl protons is presented in this paper, based on the 2D HMBC spectral analysis.

The couplings analyzed from the 2D HMBC analysis are depicted in Scheme 1, where X and Y can be either methyl acrylate or methyl methacrylate mono-

mer unit. Table I lists the coupling carbon and proton nuclei along with the respective number of couplings given in the Scheme 1.  $\alpha$ -Methyl proton resonances assigned by the 2D HSQC spectral analysis were applied to assign the methylene carbon resonances (couplings 1 and 2, in Scheme 1), quaternary carbon resonances (coupling 3), and carbonyl carbon (coupling 8). Thereby, couplings of the  $\alpha$ -methyl protons with quaternary carbon and carbonyl carbon enabled to assign the methyl methacrylate (B)-centered triads of the respective carbon resonances.

Methylene protons are equivalent for the ArA and BrB dyads but are in-equivalent for the AmA, AmB, ArB, and BmB dyads (where, m and r stands for meso and racemic, placements of the monomer units). Methylene protons assigned using 2D HSQC spectra and confirmed from the 2D TOCSY studies enabled to assign the quaternary carbon (couplings 4–7) and carbonyl carbon (couplings 9–16) resonances. The couplings reported for the poly(methyl methacrylate) HMBC spectral analysis were followed to assign the cross-peaks of BB dyad for methylene, BBB triad for methine, and quaternary and BBBB tetrad and BBBBBB hexad for the methylene units.

### Methylene carbon resonances

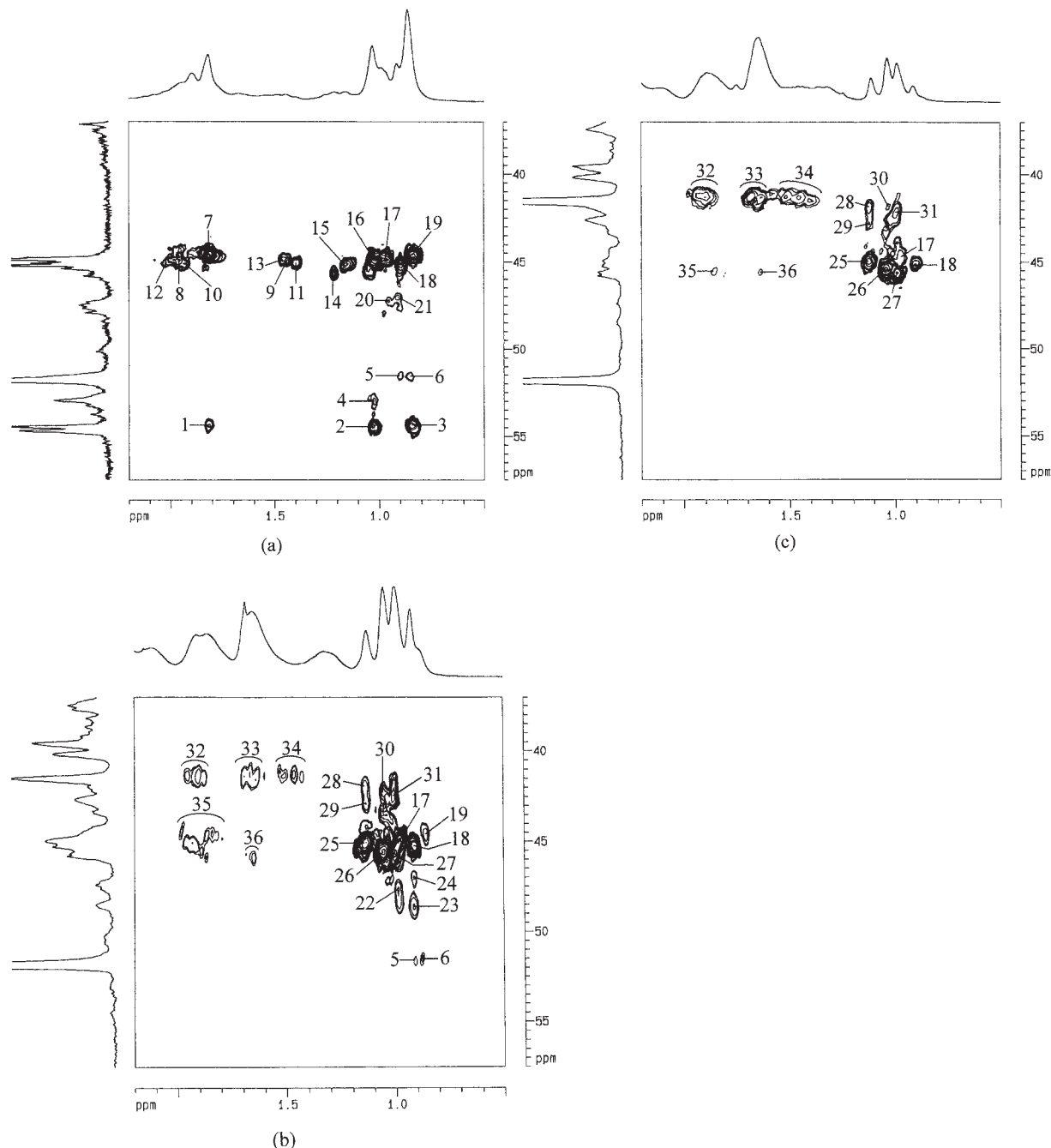
The cross-peaks observed from the 2D HMBC (Fig. 1) spectral analysis due to couplings of methylene ( $\text{CH}_2$ ) carbon with  $\alpha$ -methyl ( $\alpha\text{-CH}_3$ ) protons and methylene protons are listed in Table II. The methylene carbon in BrBrBrB tetrad showed coupling with the methylene proton of BrBrBrB tetrad in the BrBrBrBrB pentad, giving cross-peak 1 [Fig. 1(a)]. Protons of the  $\alpha$ -methyl group in BmBrB triad couple with methylene carbons of BrBmBrB and BmBrBrB tetrads giving cross-peaks 2 and 4, respectively. The  $\alpha$ -methyl protons of the BrBrB triad couple with the methylene carbons of the BrBrBrB and BBBA tetrads to give cross-peaks 3 and 5, respectively.

The BrBA  $\alpha$ -methyl protons can show couplings with the methylene resonances having BBA triad included in the respective tetrads. Thus, in the BABB and ABBA tetrads methylene carbon can couple with the  $\alpha$ -methyl protons of BBA triads. On this basis,

**TABLE I**  
Couplings Depicted in the Scheme 1

Carbon nuclei	Proton nuclei	No. of the Coupling(s) <sup>a</sup>
Methylene	$\alpha$ -Methyl	1, 2
Quaternary	$\alpha$ -Methyl	3
Quaternary	Methylene	4, 5, 6, 7
Carbonyl	$\alpha$ -Methyl	8
Carbonyl	Methylene	9, 10, 11, 12, 13, 14, 15, 16

<sup>a</sup> Number of the coupling(s) correspond to the respective couplings shown in Scheme 1.



**Figure 1** 2D HMBC NMR spectra of the methyl acrylate (A)/methyl methacrylate (B) copolymers in  $\text{CDCl}_3$ . (a)  $F_A = 0.092$ , (b)  $F_A = 0.579$ , and (c)  $F_A = 0.761$  showing the methylene, quaternary, and methine carbon couplings.

cross-peaks 20, 21, 22, and 24 were assigned to the couplings between  $\alpha$ -methyl protons of the BrBA triads with the methylene carbon centered in the BABB tetrad. The cross-peak 23 was assigned to the coupling of  $\alpha$ -methyl protons of BrBA triad with the methylene carbon of the ABBA tetrad [Fig. 1(b)].

The  $\alpha$ -methyl protons of the ABA triad can couple with the methylene carbon of the AABA and BABA tetrads containing the ABA unit. The  $\alpha$ -methyl protons of the ABA triad units showed the couplings with

the AABA methylene carbon as cross-peaks 28, 29, 30, and 31 [Fig. 1(b,c)]. The analysis of the cross-peaks thus enabled to confirm the assignments of the methylene carbon resonances done from the 2D HSQC and 2D TOCSY NMR studies.<sup>17</sup>

#### Quaternary carbon resonances

The cross-peaks observed from the 2D HMBC spectral (Fig. 1) analysis due to couplings of quaternary ( $4^\circ$ )

**TABLE II**  
**Couplings of Methylene (CH<sub>2</sub>) and Quaternary (4°) Carbon With  $\alpha$ -Methyl ( $\alpha$ -CH<sub>3</sub>) and Methylene Protons Observed From the 2D HMBC Spectra**

Cross-peak No.	Carbon nuclei	Proton nuclei	Cross-peak position(ppm)
1	CH <sub>2</sub> BrBrBrB	CH <sub>2</sub> BrBrBrB	54.5/1.82
2	CH <sub>2</sub> BrBmBrB	$\alpha$ -CH <sub>3</sub> BmBrB	54.4/1.02
3	CH <sub>2</sub> BrBrBrB	$\alpha$ -CH <sub>3</sub> BrBrB	54.5/0.87
4	CH <sub>2</sub> BmBrBrB	$\alpha$ -CH <sub>3</sub> BmBrB	53.0/1.02
5	CH <sub>2</sub> BBBA	$\alpha$ -CH <sub>3</sub> BrBA	51.5/0.92
6	CH <sub>2</sub> BBBA	$\alpha$ -CH <sub>3</sub> BrBrB	51.5/0.87
7	4° BrBrB	CH <sub>2</sub> BrBrBrB	44.7/1.81
8	4° BrBmB	CH <sub>2</sub> BmBrBmBrBrB (Ha)	45.0/1.98
9	4° BrBmB	CH <sub>2</sub> BmBrBmBrBrB (Hb)	45.0/1.44
10	4° BrBmB	CH <sub>2</sub> BrBrBmBrBrB (Ha)	45.0/1.94
11	4° BrBmB	CH <sub>2</sub> BrBrBmBrBrB (Hb)	45.0/1.40
12	4° BrBmB	CH <sub>2</sub> BmBmBrB (Ha)	45.0/2.06
13	4° BrBmB	CH <sub>2</sub> BmBmBrB (Hb)	45.0/1.46
14	4° BmBmB	$\alpha$ -CH <sub>3</sub> BmBmB	45.7/1.20
15	4° BBA	$\alpha$ -CH <sub>3</sub> BmBA	45.1/1.16
16	4° BrBmB	$\alpha$ -CH <sub>3</sub> BmBrB	45.0/1.02
17	4° BBA	$\alpha$ -CH <sub>3</sub> BrBA	45.0/0.91
18	4° BBA	$\alpha$ -CH <sub>3</sub> BrBA	45.0/0.99
19	4° BrBrB	$\alpha$ -CH <sub>3</sub> BrBrB	44.7/0.87
20	CH <sub>2</sub> BABB	$\alpha$ -CH <sub>3</sub> BrBA	47.3/0.91
21	CH <sub>2</sub> BABB	$\alpha$ -CH <sub>3</sub> BrBA	47.0/0.99
22	CH <sub>2</sub> BABB	$\alpha$ -CH <sub>3</sub> BrBA	47.6/0.99
23	CH <sub>2</sub> ABBA	$\alpha$ -CH <sub>3</sub> BrBA	48.5/0.91
24	CH <sub>2</sub> BABB	$\alpha$ -CH <sub>3</sub> BrBA	47.0/0.91
25	4° ABA	$\alpha$ -CH <sub>3</sub> ABA	44.9/1.12
26	4° ABA	$\alpha$ -CH <sub>3</sub> ABA	45.4/1.06
27	4° ABA	$\alpha$ -CH <sub>3</sub> ABA	45.5/1.00
28	CH <sub>2</sub> AABA	$\alpha$ -CH <sub>3</sub> ABA	41.9/1.12
29	CH <sub>2</sub> AABA	$\alpha$ -CH <sub>3</sub> ABA	42.8/1.12
30	CH <sub>2</sub> AABA	$\alpha$ -CH <sub>3</sub> ABA	42.2/1.06
31	CH <sub>2</sub> AABA	$\alpha$ -CH <sub>3</sub> ABA	42.4/1.00

carbon with  $\alpha$ -methyl ( $\alpha$ -CH<sub>3</sub>) protons and methylene protons are listed in Table II. Methylene protons, Ha and Hb, of the BmBrBmBrBrB hexad couple with the quaternary carbon of BrBmB triad to give rise to the cross-peaks 8 and 9, respectively. This class of couplings has been depicted in the Scheme 1 as couplings 4, 5, 6, and 7 [Fig. 1(a)]. The BrBrBmBrBrB methylene Ha and Hb protons couple with the quaternary carbon of BrBmB triad to give rise to the cross-peaks 10 and 11, respectively. Similarly, methylene protons, Ha and Hb, of BmBmBrB tetrad couple with quaternary carbon of the BmBrB triads giving rise to cross-peaks 12 and 13, respectively.

The  $\alpha$ -methyl protons of the BmBmB triad couple with the quaternary carbon of same B monomer unit in BmBmB triad to give cross-peak 14. The quaternary carbons in the BmBmB, BBA, BrBmB, BrBrB, and ABA triads were assigned by analyzing their couplings with the respective  $\alpha$ -methyl protons. The corresponding cross-peaks 14, 15, 16, 17, 18, 19, 25, 26, and 27 are shown in Figure 1 and listed in the Table II. Thereby, by the application of 2D HMBC spectroscopy along with the assignments done by 2D HSQC and confirmed by the 2D TOCSY spectroscopy, quaternary

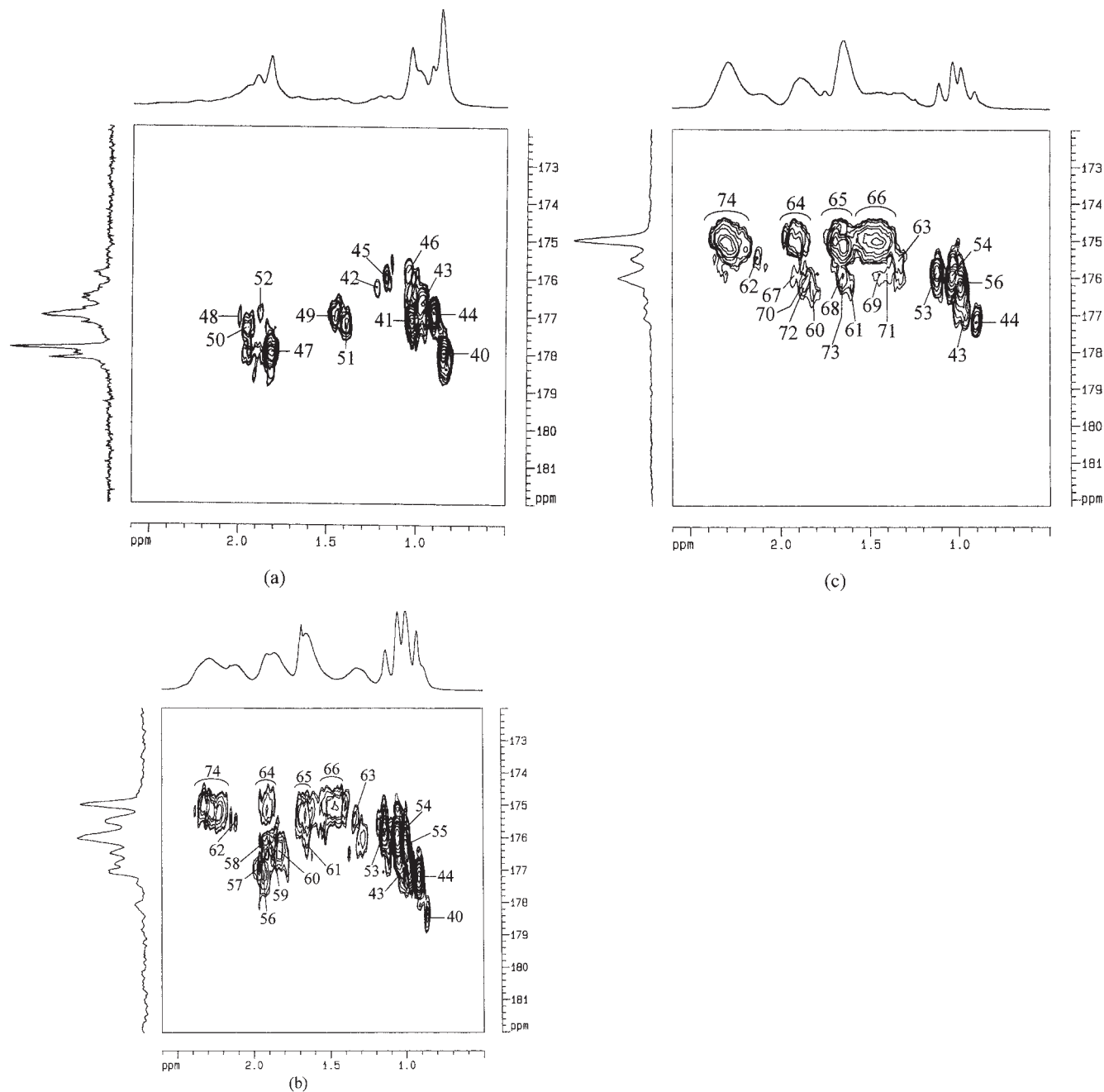
carbon resonances were assigned. The cross-peaks 35 and 36 were assigned to the couplings between the methylene protons, Ha and Hb, of the ArB unit with the methylene carbons of the BABA and BBAA tetrad.

#### Methine carbon resonances

The cross-peaks 32, 33, and 34 [Fig. 1(b,c)] were assigned to the couplings between the methine carbon of the AAA triad with the methylene protons of the AmA (Ha), ArA, and AmA (Hb), respectively.

#### Carbonyl carbon resonances

Assignments of the carbonyl carbon resonances of acrylate copolymers is a complicated and speculative procedure. To assign the carbonyl carbon resonances evidently, the analysis of couplings between the carbonyl carbon and the  $\alpha$ -methyl protons and methylene protons were analyzed. The  $\alpha$ -methyl protons of the B monomer unit will have 1,3 bond order couplings with the carbonyl carbon, shown as coupling 8 in Scheme 1, enabling to assign the B-centered triads. The



**Figure 2** 2D HMBC NMR spectra of the methyl acrylate (A)/methyl methacrylate (B) copolymers in  $\text{CDCl}_3$ . (a)  $F_A = 0.092$ , (b)  $F_A = 0.579$ , and (c)  $F_A = 0.761$  showing the carbonyl carbon couplings.

methylene protons showing 1,3 bond order couplings (shown as couplings 9–16 in Scheme 1) with the carbonyl carbon enabled to assign the A-centered triads as well.

2D HMBC spectra showing the carbonyl carbon couplings with the  $\alpha$ -methyl protons and the methylene carbon are given in Figure 2. The  $\alpha$ -methyl proton resonances of the BrBrB, BrBmB, and BmBmB triads showed couplings with the carbonyl carbon of the same triads enabling the assignment of the respective carbon resonances (Table III). The cross-peaks 40, 41,

and 42 were thus assigned to the BrBrB, BrBmB, and BmBmB triads, respectively. The carbonyl carbon spectra of the different compositions, assigned with the help of 2D HMBC spectral analysis, are shown in Figure 3.

The  $\alpha$ -methyl proton resonances of the BrBA showed cross-peaks 43 and 44 on coupling with the carbonyl carbon of the BrBA triad. Similarly,  $\alpha$ -methyl proton resonances of the BmBA triad showing cross-peaks facilitated to assign the BmBA carbonyl carbon reso-

**TABLE III**  
**Couplings of Carbonyl Carbon With  $\alpha$ -Methyl Protons ( $\alpha$ -CH<sub>3</sub>) and Methylene Protons Observed From the 2D HMBC Spectra**

Cross-peak No.	Carbon nuclei	Proton nuclei	Cross-peak position (ppm)
40	BrBrB	$\alpha$ -CH <sub>3</sub> BrBrB	177.9/0.86
41	BrBmB	$\alpha$ -CH <sub>3</sub> BrBmB	177.1/1.03
42	BmBmB	$\alpha$ -CH <sub>3</sub> BmBmB	176.2/1.22
43	BrBA	$\alpha$ -CH <sub>3</sub> BrBA	176.6/0.99
44	BrBA	$\alpha$ -CH <sub>3</sub> BrBA	176.9/0.91
45	BmBA	$\alpha$ -CH <sub>3</sub> BmBA	176.0/1.17
46	BmBA	$\alpha$ -CH <sub>3</sub> BmBA	175.7/1.05
47	BrBrB	CH <sub>2</sub> BrBrBrB	178.0/1.81
48	BrBmB	CH <sub>2</sub> BmBrBmBrBrB (Ha)	177.0/2.00
49	BrBmB	CH <sub>2</sub> BmBrBmBrBrB (Hb)	177.0/1.45
50	BrBmB	CH <sub>2</sub> BrBrBmBrBrB (Ha)	177.2/1.96
51	BrBmB	CH <sub>2</sub> BrBrBmBrBrB (Hb)	177.1/1.40
52	BrBA	CH <sub>2</sub> BBBA	176.9/1.84
53	ABA	$\alpha$ -CH <sub>3</sub> ABA	175.8/1.14
54	ABA	$\alpha$ -CH <sub>3</sub> ABA	175.9/1.05
55	ABA	$\alpha$ -CH <sub>3</sub> ABA	176.1/1.00
56	ABrB	CH <sub>2</sub> ABBA	177.1/1.92
57	ABrB	CH <sub>2</sub> ABBA	177.0/1.96
58	ABmB	CH <sub>2</sub> ABBA	176.1/1.92
59	ABmB	CH <sub>2</sub> ABBA	176.1/1.86
60	BArB	CH <sub>2</sub> BArBA (Ha)	176.4/1.82
61	BArB	CH <sub>2</sub> BArBA (Hb)	176.3/1.64
62	AAmB	CH <sub>2</sub> AAmBA (Ha)	175.4/2.12
63	AAmB	CH <sub>2</sub> AAmBA (Hb)	175.4/1.33
64	AAA	CH <sub>2</sub> AmA (Ha)	174.7/1.9
65	AAA	CH <sub>2</sub> ArA	174.7/1.65
66	AAA	CH <sub>2</sub> AmA (Hb)	174.7/1.4
67	AmAB	CH <sub>2</sub> AAmAB (Ha)	175.9/1.91
68	ArAB	CH <sub>2</sub> AArAB/BArAB	175.9/1.64
69	AmAB	CH <sub>2</sub> AAmAB (Hb)	175.9/1.44
70	AmAB	CH <sub>2</sub> BAmAB (Ha)	175.9/1.84
71	AmAB	CH <sub>2</sub> BAmAB (Hb)	175.9/1.39
72	AArB	CH <sub>2</sub> AArBA (Ha)	176.1/1.85
73	AArB	CH <sub>2</sub> AArBA (Hb)	176.1/1.65

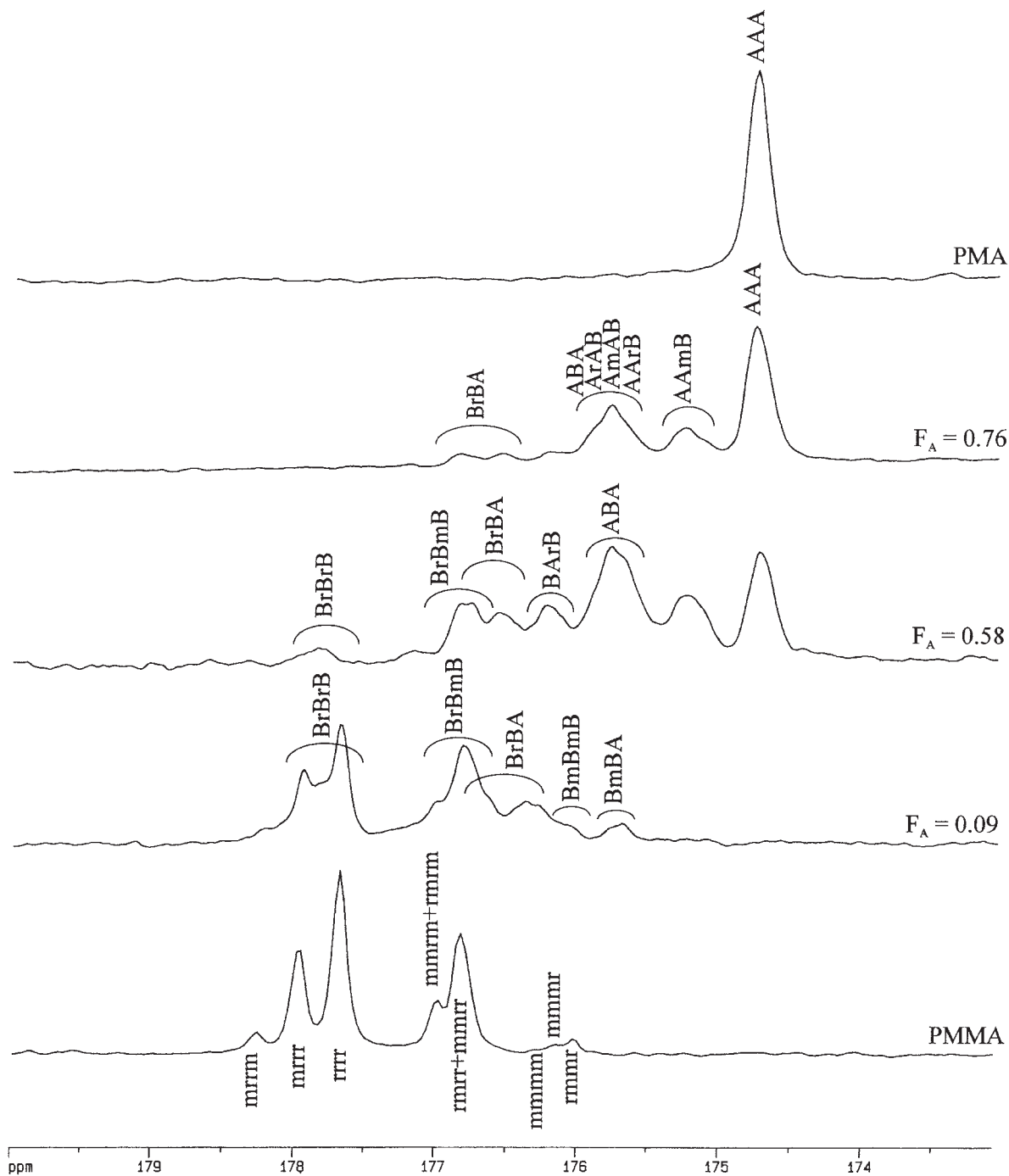
nances. BmBA triad has low concentration owing to having a "meso" placement and is difficult to assign using 1D NMR experiments only. Such assignments show the pivotal role that 2D NMR plays in the studies of the polymer microstructure. Likewise, couplings between the  $\alpha$ -methyl protons and carbonyl carbon in the ABA triad were assigned to the cross-peaks 53, 54, and 55 [Fig. 2(b,c)].

Methylene proton resonances assigned up to the tetrad level of the compositional and configurational sensitivity proved to be highly useful in the carbonyl carbon assignments. On the basis of the assignments of the poly(methyl methacrylate), the assignments of the cross-peaks of the BBBB tetrads were done, as shown in Figure 2(a). Coupling between the methylene protons of the BrBrBrB tetrad and the carbonyl carbon of the BrBrB resulted in the cross-peak 47. The methylene protons, Ha and Hb, of the BmBrBmBrBrB hexad coupled with carbonyl carbon of the BrBmB triad giving cross-peaks 48 and 49, respectively. Similarly, cross-peaks 50 and 51 were assigned to the

couplings between Ha and Hb of BrBrBmBrBrB hexad and carbonyl carbon of the BrBmB triad.

After analyzing the assignments of carbonyl carbon, it was observed that the meso-centered BB dyad was having lower chemical shift value than that of BrB dyad. Thus, with the aid of this trend and 2D HMBC analysis, rest of the carbonyl carbon resonances were assigned. Methylene protons of the ABBA tetrad can couple with the carbonyl carbon of both ABrB and ABmB triads. The HMBC spectra [Fig. 2(b)] was showing two cross-peaks corresponding to the methylene protons of ABBA tetrads, one at 177.1 ppm and another at 176.1 ppm. Following the chemical shift trend, the cross-peak 56 at higher chemical shift on carbon axis was assigned to the coupling between methylene protons of the ABBA tetrad with carbonyl carbon of the ABrB triad. Thus, the cross-peak 58 having lower chemical shift on the carbon axis was assigned to the carbonyl carbon of the ABmB triad.

Again, methylene protons of the ABBA tetrad can show couplings to both the ABmB and ABrB triads.



**Figure 3** Assigned carbonyl carbon resonances of PMA (poly(methyl acrylate)), methyl acrylate (A)/methyl methacrylate (B) copolymers of different compositions and PMMA (poly(methyl methacrylate)).

Following the logic presented above, carbonyl carbon of the ABrB triad was assigned to the cross-peak 57 having higher chemical shift of 177.0 on the carbon axis. Similarly, the cross-peak 59 having lower chemical shift value on the carbon axis, 176.1 ppm, was assigned to the ABmB triads. The assignments of the ABrB and ABmB triad made from the analysis of methylene proton couplings of ABBA and ABBB tetrad were same, thus establishing the assignments made.

The methylene protons Ha and Hb of the BArBA tetrad can couple with the carbonyl carbon of the BArB and ArBA triads. Methylene protons of the BArBA tetrad showed cross-peaks 60 and 61 [Fig. 2(b,c)] at 176.4 and 176.3 ppm on the carbon axis, which were at higher chemical shifts than those assigned to the ABA triads previously (175.8, 175.9, and 176.1 ppm). Thus the cross-peaks 60 and 61 corresponding to the methylene protons, Ha and Hb, of the BArBA tetrads were assigned to the BArB triads.

The methylene protons, Ha and Hb, of the AAmBA tetrads can show couplings with the carbonyl carbon of the AAmB and AmBA triads. Two cross-peaks 62 and 63 [Fig. 2(b,c)] were corresponding to the AAmBA tetrads, but being at lower chemical shifts (175.4 ppm) than that of ABA triads, were assigned to the couplings between methylene protons, Ha and Hb, of AAmBA tetrad with the carbonyl carbon of the AAmB triad.

The cross-peaks 64, 65, and 66 [Fig. 2(b,c)] were assigned to the couplings between AmA (Ha), ArA and AmA (Hb), methylene protons and carbonyl carbon of the AAA triad. Methylene protons, Ha and Hb, of the AAmAB tetrads can couple with the carbonyl carbon of the AAA and AmAB triad. The chemical shift of the carbonyl carbon of the AAA triad was not matching with the chemical shifts of the cross-peaks corresponding to the AAmAB tetrads. Thus, the cross-peaks 67 and 69 [Fig. 2(c)] were assigned to the couplings between Ha and Hb of the AAmAB tetrad with the carbonyl carbon of the AmAB triad. Similarly, the cross-peak 68 was assigned to the coupling between the methylene protons of the AArAB/BArAB with the carbonyl carbon of the ArAB triad. The couplings between the methylene protons Ha and Hb of the BAmAB tetrad with the carbonyl carbon of the BAmA triad resulted in the cross-peaks 70 and 71. The inequivalent methylene protons, Ha and Hb, of the AArBA resulted in cross-peaks 72 and 73 due to the couplings with the carbonyl carbon of the AArB triad.

The completely assigned carbonyl carbon region, based on the 2D HMBC spectral analysis, of the methyl methacrylate/methyl acrylate copolymers is shown in the Figure 3.

### CONCLUSIONS

A detailed 2D HMBC spectral analysis of methyl acrylate (A)/methyl methacrylate (B) copolymers was done. The methylene carbon and methine carbon resonances assigned from the 2D HSQC spectroscopy were established by analyzing the two and three bond order couplings with  $\alpha$ -methyl protons, methylene

protons, and methine protons. Quaternary carbon resonances were assigned by investigating the two bond order couplings with  $\alpha$ -methyl protons and methylene protons at triad level. Assignments of carbonyl carbon resonances based on the analysis of three bond couplings with  $\alpha$ -methyl protons and methylene protons are reported. The analysis presents comprehensive assignments of the carbonyl carbon resonances showing the critical contribution of 2D HMBC spectroscopy in the indirect analysis of carbon resonances. The 2D HSQC and TOCSY experiments in conjugation with the 2D HMBC experiments proved to be highly informative and irrefutable methodology for the microstructure analysis of polymers.

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