

# Stereochemical Elucidation of Complex $\alpha$ -Methyl and $\beta$ -Methylene Carbon Resonances in Poly(2-hydroxy ethyl methacrylate-co-methacrylonitrile) by 2D NMR

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**ABSTRACT:** Copolymers of 2-hydroxy ethyl methacrylate and methacrylonitrile (H/M) of different composition were synthesized by free radical bulk polymerization using azobisisobutyronitrile (AIBN) as an initiator under nitrogen atmosphere. The copolymers composition were calculated from  $^1\text{H}$  and quantitative  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra. The complete spectral assignment of complex and overlapped  $\alpha$ -methyl and  $\beta$ -methylene carbon regions in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum in term of compositional and con-

figurational sequences of H/M copolymers were done with the help of two-dimensional heteronuclear single quantum coherence (HSQC) and total correlation spectroscopy (TOCSY). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2381–2386, 2009

**Key words:** 2-hydroxy ethyl methacrylate; methacrylonitrile; copolymerization; microstructure; NMR; configuration

## INTRODUCTION

Over the last few decades, hydrophilically modified polymers have attracted increasing interest owing to their practical and fundamental importance.<sup>1,2</sup> The strong viscosifying ability as well as macroscopical rheology features enables the attraction of these polymers to various industrial uses, where the control of fluid rheology is required, for example, coating, paints, cosmetics, drilling fluid, petroleum recovery, and foods. The physically linked viscoelastic gel can have application in drug release and control, as agricultural agents, and as adsorbents in separation processes.<sup>3,4</sup> NMR spectroscopy plays a significant role in the structure elucidation of polymers.<sup>5,6</sup> 1D NMR in conjugation with 2D technique furnishes a very efficient method for studying the microstructure of polymers. 2D NMR spectroscopy has become a very important and valuable technique for determining the polymeric structure. 2D HSQC along with 2D TOCSY provides a correlation between  $^1\text{H}$  and  $^{13}\text{C}$  nuclei that are one bond apart in polymeric chain.<sup>7–9</sup> Various coworkers have reported the controlled polymerization of poly(2-hydroxy ethyl methacrylate) and its copolymers.<sup>10–12</sup> Thermal behavior and

microstructural studies of poly(methacrylonitrile) and its copolymers were done earlier.<sup>13,14</sup> Brar et al. have well reported the reactivity ratios and microstructure of methacrylonitrile copolymers with other vinyl monomers.<sup>15–17</sup> To the best of our knowledge, stereochemical assignments of complex and overlapped NMR spectrum of 2-hydroxy ethyl methacrylate-methacrylonitrile (H/M) copolymers has not been reported so far. In this manuscript, we report the microstructure of 2-hydroxy ethyl methacrylate and methacrylonitrile (H/M) copolymers. The complete  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectral assignments of 2-hydroxy ethyl methacrylate and methacrylonitrile (H/M) copolymers were done with the help of 2D HSQC and TOCSY NMR experiments.

## EXPERIMENTAL

2-Hydroxy ethyl methacrylate and methacrylonitrile (H/M) monomers were distilled under reduced pressure and stored below 5°C. A series of H/M copolymers of different composition were prepared by bulk polymerization using AIBN as an initiator at 70°C under nitrogen atmosphere. The percent conversion was kept below 10% by precipitating the copolymers in hexane. The copolymers were further purified using methanol/hexane system for higher composition of H-unit and chloroform/hexane for lower composition of H-unit in copolymer. The recording of all NMR spectra have been explained elsewhere.<sup>18</sup>

## RESULTS AND DISCUSSION

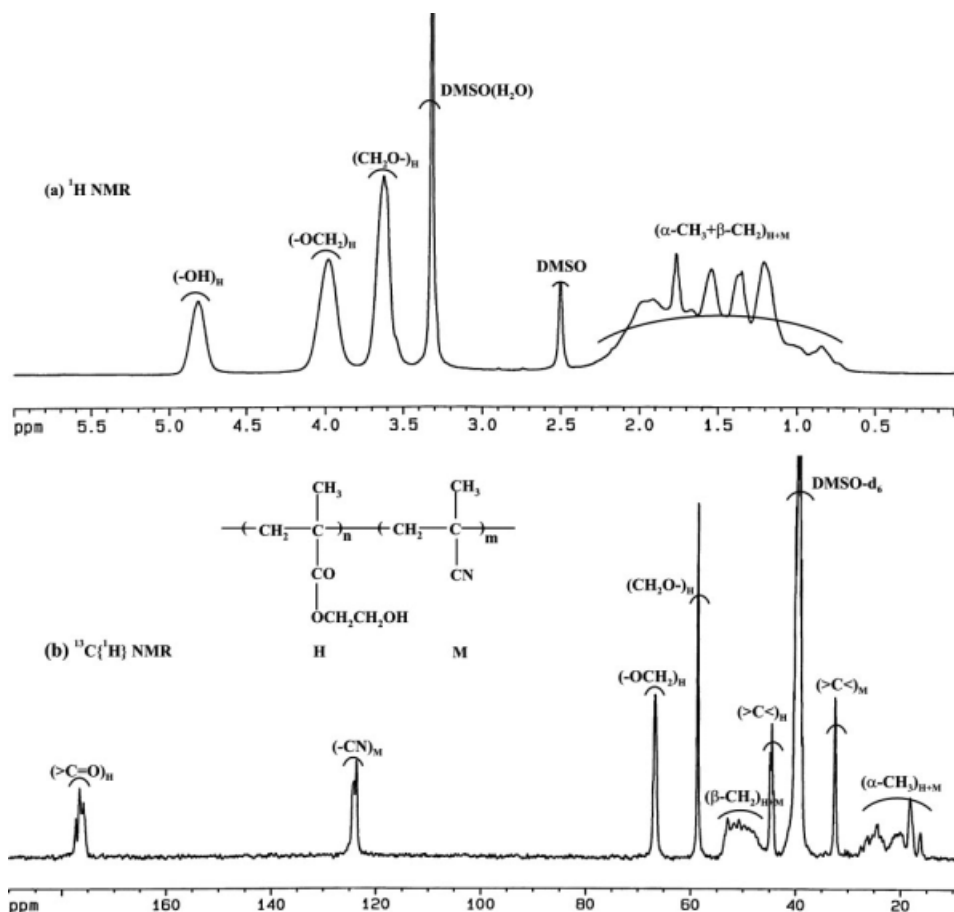
### Copolymer composition determination

The composition of H/M copolymers was determined from completely assigned  $^1\text{H}$  NMR spectrum

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**Figure 1** (a) The  $^1\text{H}$  and (b)  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of H/M copolymer ( $F_H = 0.47$ ) in  $\text{DMSO-}d_6$  at  $80^\circ\text{C}$ .

[Fig. 1(a)]. The intensity of  $-\text{OH}$  proton of H-unit and combined intensity of  $\alpha$ -methyl and  $\beta$ -methylene protons of both units were used for the determination of copolymers composition as given in following equation:

$$F_H = \frac{I(-\text{OH})_H}{I(\alpha-\text{CH}_3 + \beta-\text{CH}_2)_{H+M}/5}$$

where  $F_H$  represents the composition of H-unit in the copolymer while  $I(\text{OH})_H$  represents the intensity of  $-\text{OH}$  proton of H-unit and  $I(\alpha-\text{CH}_3 + \beta-\text{CH}_2)_{H+M}$  represents the combined intensity of  $\alpha$ -methyl and  $\beta$ -methylene protons of both H- and M-units, respectively. The copolymer composition was further confirmed by quantitative  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra [Fig. 1(b)]. The copolymers composition data of H/M copolymer is given in Table I.

## 2D NMR studies

The broad and overlapped resonance signals of copolymers which were not resolved by one-dimensional experiments [ $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and distortionless enhancement by polarization transfer (DEPT)] can be assigned completely to various compositional and

configurational sequences by two-dimensional heteronuclear single quantum coherence (HSQC) and total correlation spectroscopy (TOCSY). 2D HSQC NMR study shows one-to-one correlation between carbon and proton signals while 2D TOCSY spectra were used to confirm 1, 2 bond geminal couplings between nonequivalent protons of the same methylene group.

## $\alpha$ -Methyl carbon resonances

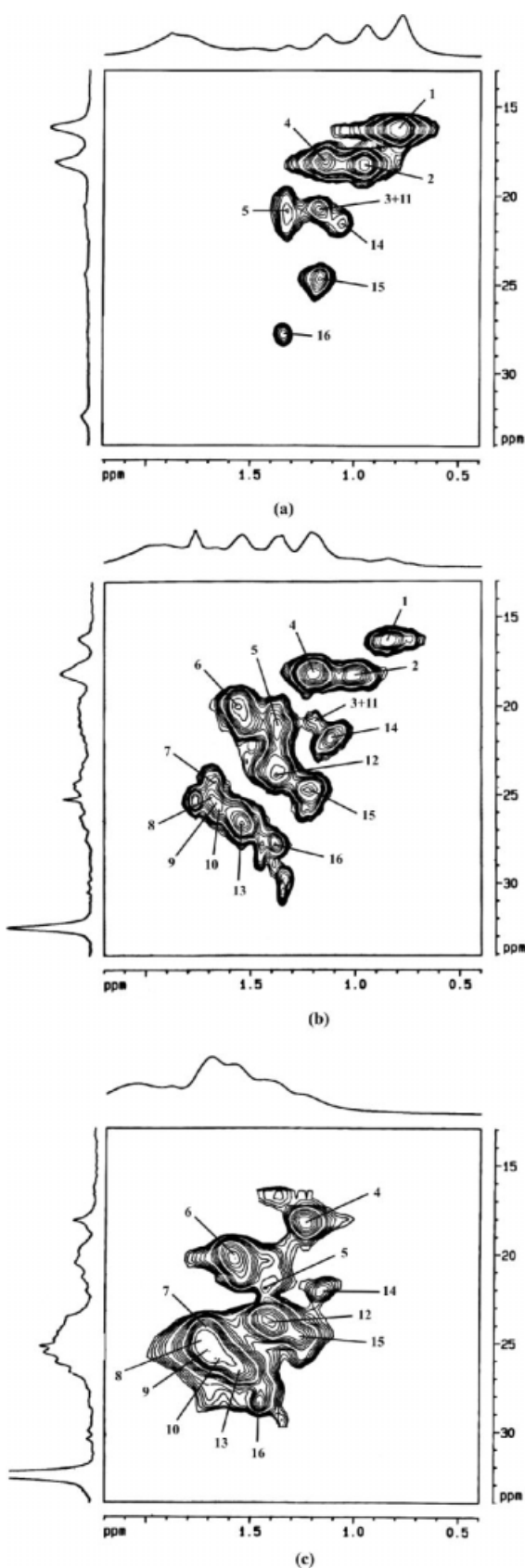
The expanded overlapped  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of  $\alpha$ -methyl carbon region of both H- and M-units of H/M copolymers along with poly(2-hydroxy ethyl

**TABLE I**  
Copolymer Composition Data of H/M Copolymers

S. No.	Sample no.	$f_H$	$F_H$
1.	HM2	0.20	0.24
2.	HM3	0.30	0.32
3.	HM5	0.50	0.47
4.	HM7	0.70	0.64
5.	HM9	0.90	0.86

$f_H$  is the mole fraction of H-comonomer in feed and  $F_H$  is the mole fraction of H-comonomer in copolymer.





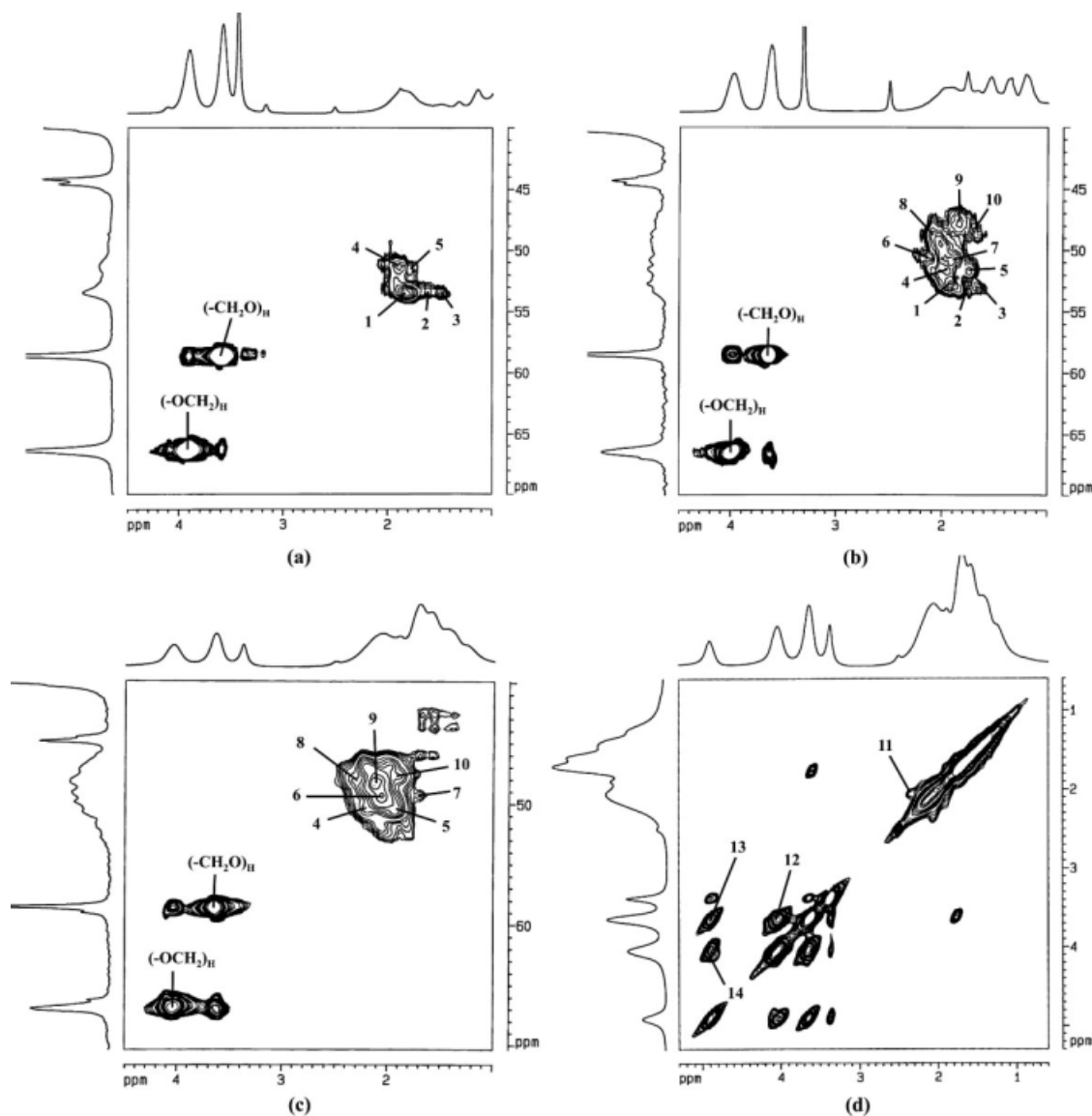
**Figure 3** The expanded  $\alpha$ -methyl carbon region of 2D HSQC spectra of H/M copolymers with compositions ( $F_H =$ ): (a) 0.86, (b) 0.47, (c) 0.24 in DMSO- $d_6$  at 80°C.

respectively. Similarly, cross peaks 14, 15, and 16 are assigned to HrMrH, HrMmH, and HmMmH triads, respectively. All the assignments are given in Table II. Based on 2D HSQC spectral assignments, the complex and overlapped  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were resolved completely. The overlapped multiplet in methyl carbon region is assigned to both the compositional and configurational sequences. The assignments of various signals have been carried out with the help of spectra of poly(2-hydroxy ethyl methacrylate), poly(methacrylonitrile) and by observing change in intensity of signals with change in composition of copolymers.

In  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (Fig. 2), the resonance signal I is assigned to HrHrH triad on comparison with poly(2-hydroxy ethyl methacrylate). Since the intensity of signal II in copolymers is more than PHEMA signal, this resonance signal is assigned to the overlap of HrHrM and HrHmH triads. The signal III appeared on further increasing the concentration of M-unit and its intensity increases with increase in concentration of M-unit. So this signal was assigned to the overlap of HrHmM, HmHmH, MrHrM, HrMrM, and HrMrH triads. The intensity of resonance signal IV is low and almost remains the same in Figure 2(c,d) as it is the overlap of all M-centered compositional and configurational sequences, i.e., MrMrM, MrMmM, MmMmM, MrMmH, HrMmH, MrHmM, and MmMmH triads [Fig. 2(d)], while the resonance signal V is assigned to HmMmH triad. In M-centered methyl carbon, the addition of H-unit causes shielding effect but the change of configuration from rr, mr, and mm triads causes deshielding effect, while in the case of H-centered triads,

**TABLE II**  
Assignments of  $\alpha$ -CH<sub>3</sub> Carbon Resonances of H/M Copolymers from 2D HSQC Spectra

Peak no.	Peak assignments	Peak position, 2D HSQC ( $^{13}\text{C}/^1\text{H}$ ; ppm)
1.	HrHrH	16.04/0.83
2.	HrHmH	18.02/0.99
3.	HmHmH	20.97/1.17
4.	HrHrM	18.00/1.15
5.	HrHmM/HmHrM	21.50/1.28
6.	MrHrM	20.04/1.56
7.	MrHmM	23.98/1.68
8.	MrMrM	25.00/1.75
9.	MmMrM	25.46/1.70
10.	MmMmM	25.90/1.65
11.	MrMrH	18.02/0.99
12.	MrMmH/MmMrH	23.90/1.45
13.	MmMmH	26.50/1.55
14.	HrMrH	22.04/1.17
15.	HrMmH	24.58/1.28
16.	HmMmH	28.00/1.40



**Figure 4** The expanded 2D HSQC spectra of H/M copolymers containing  $\beta$ -methylene carbon region with compositions ( $F_H =$ ): (a) 0.86, (b) 0.47, (c) 0.24, and (d) 2D TOCSY spectrum containing  $F_H = 0.87$  in DMSO- $d_6$  at 80°C.

addition of M-unit as well as the change of configurations from rr, rm to mm causes the downfield shift.

#### $\beta$ -Methylene carbon resonances

The resonance signal around  $\delta$  45.0–55.0 ppm in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum [Fig. 1(b)] was assigned to the overlap of  $\beta$ -methylene carbon of both H- and M-unit. This resonance signal was resolved completely with the help of 2D HSQC spectra. The protons in the racemic configuration are in same environment, resulting in a single cross peak in 2D HSQC spectra. The two nonequivalent methylene protons in meso configuration result in two cross peaks in 2D HSQC spectra and a cross correlation peak in 2D TOCSY spectra. Thus, 2D TOCSY spectra

enable to differentiate between the meso and racemic protons and confirm the 2D HSQC assignments. The expanded  $\beta$ -methylene region in 2D HSQC and 2D TOCSY spectra are given in the Figure 4 and the assignments are listed in Table III.

The cross peaks 1 and 3 are assigned to HmH(Ha) and HmH(Hb) diads, respectively, while HrH diad is assigned to cross peak 2. The methylene protons Ha and Hb of both HmM and HrM diads are in different magnetic environment, and thus it results in two cross peaks by coupling with methylene carbon in 2D HSQC spectra. HM diad concentration decreases with increase in composition of M-unit, on this basis HM diad is assigned. HmM(Ha) and HmM(Hb) diads are assigned to the cross peaks 4 and 5, respectively, while HrM(Ha) and HrM(Hb) diads are assigned to cross peaks 6 and 7. Similarly,

**TABLE III**  
Assignments of  $\beta$ -Methylene Carbon Resonances of H/M Copolymers from 2D HSQC and 2D TOCSY Spectra

Cross peak no.	Cross-peak assignment	Peak position, 2D HSQC ( $^{13}\text{C}/^1\text{H}$ ; ppm)
1.	HmH(Ha)	53.60/1.85
2.	HrH	53.60/1.68
3.	HmH(Hb)	53.60/1.52
4.	HmM(Ha)	51.15/2.20
5.	HmM(Hb)	51.15/1.90
6.	HrM(Ha)	49.85/2.10
7.	HrM(Hb)	49.85/1.80
8.	MmM(Ha)	48.00/2.32
9.	MrM	48.00/2.13
10.	MmM(Hb)	48.00/1.90

Cross peak no.	Proton 1/Proton 2	2D TOCSY ( $^1\text{H}(1)/^1\text{H}(2)$ ; ppm)
11.	Geminal coupling of all $\beta$ -CH <sub>2</sub> protons	2.10/2.35
12.	—CH <sub>2</sub> O/—OCH <sub>2</sub>	3.61/4.10
13.	—OCH <sub>2</sub> /—OH	4.10/4.92
14.	—CH <sub>2</sub> O/—OH	3.61/4.92

MmM (Ha), MrM, and MmM (Hb) diads are assigned to cross peaks 8, 9, and 10, respectively. All the nonequivalent methylene protons (Ha and Hb) of HmH, HmM, HrM, and MmM diads resulted in cross correlation peak 11 in 2D TOCSY spectrum in Figure 4(d). The cross peak 12 was assigned to the coupling of —CH<sub>2</sub>O proton of H-unit with —OCH<sub>2</sub> protons of H-unit, while the cross peaks 13 and 14 were assigned to the coupling of —CH<sub>2</sub>O and —OCH<sub>2</sub> protons with —OH proton of H-unit, respectively. Thus, 2D TOCSY spectra enabled to differentiate between the meso and racemic protons and confirm the 2D HSQC assignments. The methyl and methylene proton resonance signals which were overlapped and could not be assigned by  $^1\text{H}$  NMR spectra alone were assigned with the help of one-to-

one correlation between carbon and proton signals in 2D HSQC spectra.

## CONCLUSIONS

The complex and overlapped  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the copolymers were resolved with the help of 2D HSQC spectra. The complex and overlapped  $\alpha$ -methyl carbons of H- and M-units were assigned up to triad compositional and configurational sequences in  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, whereas  $\beta$ -methylene carbon resonances were assigned up to diad compositional and configurational sequences.

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