

Stereochemical Assignments of the Nuclear Magnetic Resonance Spectra of Isobornyl Acrylate/Methacrylonitrile Copolymers

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ABSTRACT: Isobornyl acrylate (B)/methacrylonitrile (N) copolymers with different compositions were synthesized by the free-radical bulk polymerization with azobisisobutyronitrile as the initiator under a nitrogen atmosphere at 70°C. The copolymer compositions were calculated from quantitative ¹³C(¹H)-NMR spectra. The reactivity ratios of the comonomers in the B/N copolymers determined from the linear Kelen–Tudos method and nonlinear error-in-variable method were $r_B = 0.66 \pm 0.11$ and $r_N = 1.54 \pm 0.22$ and $r_B = 0.74$ and $r_N = 1.65$, respectively. The complete spectral assignments of the ¹H-NMR and ¹³C(¹H)-NMR spectra were carried out with the help of distortionless enhancement by polarization transfer, two-dimensional (2D) heteronuclear single quantum coherence, and 2D total cor-

relation spectroscopy. The nitrile carbon of the N unit and the methine and OCH carbons of the B unit were assigned to triad compositional sequences, whereas the β -methylene carbons of the B and N units were assigned to the tetrad compositional and configurational sequences. The α -methyl carbon of the N unit was also assigned to the triad level of configurational and compositional sequences. Similarly, the nitrile and quaternary carbon resonances with the methine, methylene, and methyl protons were studied in detail with 2D heteronuclear multiple-bond correlation spectra. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: microstructure; NMR; polymer synthesis and characterization

INTRODUCTION

Copolymers of isobornyl acrylate (B) are of great interest in many industrial applications, for example, cosmetics,¹ coatings,² bioapplications,³ drug-delivery systems,⁴ and construction material,⁵ because of their high glass-transition temperature⁶ and hardness.^{7,8} The macroscopic properties of bulk polymers are influenced fundamentally by their chain microstructure, which can be investigated by NMR spectroscopy.^{9–11} Two-dimensional (2D) NMR spectroscopy has become a very important and valuable technique for determining polymer structure. 2D heteronuclear single quantum coherence (HSQC) and total correlation spectroscopy (TOCSY) provide a correlation between ¹H and ¹³C nuclei that are one bond apart in the polymeric chain.^{9,12,13} Various researchers have reported controlled radical polymerization of copolymers of B by atom transfer radi-

cal polymerization^{14–16} and nitroxide-mediated polymerization.¹⁷ The thermal behavior and microstructural studies of polymethacrylonitrile (PMAN) and its copolymers were reported earlier.^{18,19} Brar and coworkers^{20–22} reported the reactivity ratios and microstructure of methacrylonitrile (N) copolymers with other vinyl monomers.

To the best of our knowledge, the stereochemical assignments of complex and overlapped NMR spectra of the B/N copolymers have not yet been reported. In this study, we examined the reactivity ratios of the comonomers in the B/N copolymers using the Kelen–Tudos (KT)²³ method and the nonlinear error-in-variable²⁴ method (EVM). The compositional and configurational sequence determination of the B/N copolymers was carried out by one-dimensional (1D) and 2D NMR spectroscopy. The ¹³C(¹H)-NMR and ¹H-NMR spectra of the copolymers were quite complex and were interpreted with the help of distortionless enhancement by polarization transfer (DEPT) and 2D HSQC–NMR spectroscopy. The 2D TOCSY spectrum was used to explain the ¹H–¹H correlation in the B/N copolymers, whereas 2D heteronuclear multiple-bond correlation (HMBC) spectroscopy was used to determine the long-range interactions between different groups present in the copolymer.

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TABLE I
Copolymer Composition Data of the B/N Copolymers

Sample	Infeed (f_B)	Outfeed (F_B)
1	0.80	0.72
2	0.70	0.60
3	0.60	0.51
4	0.50	0.41
5	0.40	0.30
6	0.30	0.21

(f_B) = infeed ratio of B unit; (F_B) = outfeed ratio of B unit in B/N copolymer.

EXPERIMENTAL

B (Aldrich) was purified by vacuum distillation under reduced pressure, and N (Aldrich) was purified by ordinary distillation and stored below 5°C. The solvents were purchased from Aldrich (HPLC grade) and were used without purification. All other chemicals were used as received.

B/N copolymers containing different molar fractions of B in the feed (Table I) were synthesized by free-radical bulk polymerization at 70°C with azobisisobutronitrile as an the initiator under nitrogen atmosphere. For the synthesis of the copolymers, a stock solution containing a calculated amount of monomer and initiator was prepared and sealed with a rubber septum. The solution was purged with nitro-

gen. The sample was placed in an oil bath at 70°C for 2 h. We kept the conversion below 10% by controlling the time of polymerization (2 h). We terminated the reaction by cooling and pouring the reaction mixture into methanol. The resulting copolymer was dissolved in tetrahydrofuran, and we removed the impurities by passing the diluted reaction mixture over a column of neutral alumina (Al₂O₃). After excess solvent was evaporated, the copolymer was precipitated in methanol. The crude copolymer was further purified by dissolution in tetrahydrofuran and precipitation in methanol up to four to five times. The precipitated copolymer was dried in air. A series of copolymers with different compositions (Table I) were synthesized by the same procedure. The ¹H-NMR and ¹³C(¹H)-NMR spectra of both monomers (B and N) are shown in Figure 1. The ¹H-NMR and ¹³C(¹H)-NMR spectra of the B/N copolymer ($F_B = 0.41$) in CDCl₃ are shown in Figures 2 and 3(a), respectively. A comparison of the NMR spectra of the monomers and polymer showed that the polymerization took place. In the monomers, olefinic H appeared at δ values of 5.5–6.8, whereas with polymerization, these Hs became saturated and appeared at δ values of 1.4–2.1. Similar behavior was observed in the ¹³C(¹H)-NMR spectra of both monomers, whereas the methylene carbon appeared at δ values of 127–130 and appeared at an upfield position after polymerization and gave overlapped resonance

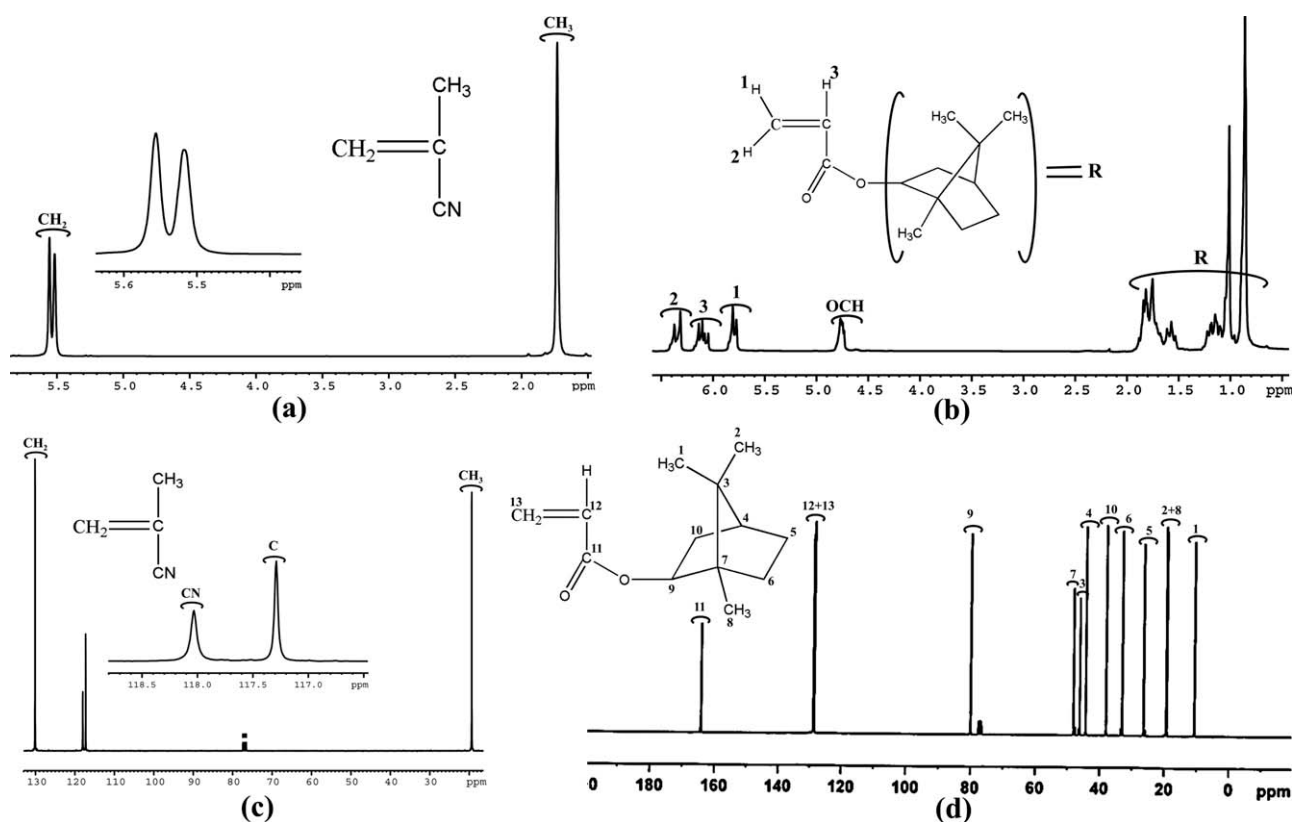


Figure 1 (a) ¹H-NMR spectrum of the N monomer, (b) ¹H-NMR spectrum of the B monomer, (c) ¹³C(¹H)-NMR spectrum of the N monomer, and (d) ¹³C(¹H)-NMR spectrum of the B monomer in CDCl₃ at 25°C.

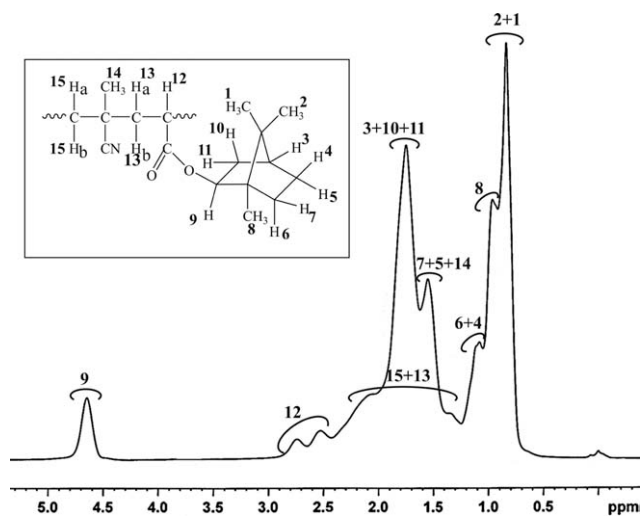


Figure 2 ^1H -NMR spectrum of the B/N copolymer ($F_B = 0.41$) in CDCl_3 at 25°C .

signals around δ values of 34.5–49.7, as shown in Figures 2 and 3(a).

NMR measurements

The 1D [^1H , $^{13}\text{C}(^1\text{H})$], and DEPT-135] and 2D (HSQC and TOCSY) NMR spectra of the B/N copolymers were recorded at 25°C in CDCl_3 with a Bruker 300-MHz DPX spectrometer with different standard pulse sequences.^{25,26}

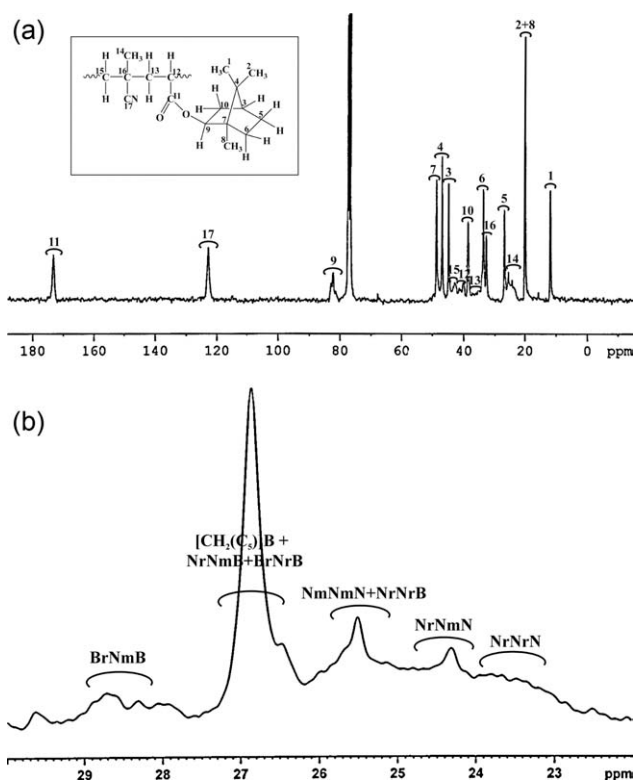


Figure 3 (a) $^{13}\text{C}(^1\text{H})$ -NMR spectrum of the B/N copolymer ($F_B = 0.41$) in CDCl_3 at 25°C . (b) Expanded α -methyl region of the $^{13}\text{C}(^1\text{H})$ -NMR spectrum of the B/N copolymer ($F_B = 0.41$) in CDCl_3 at 25°C .

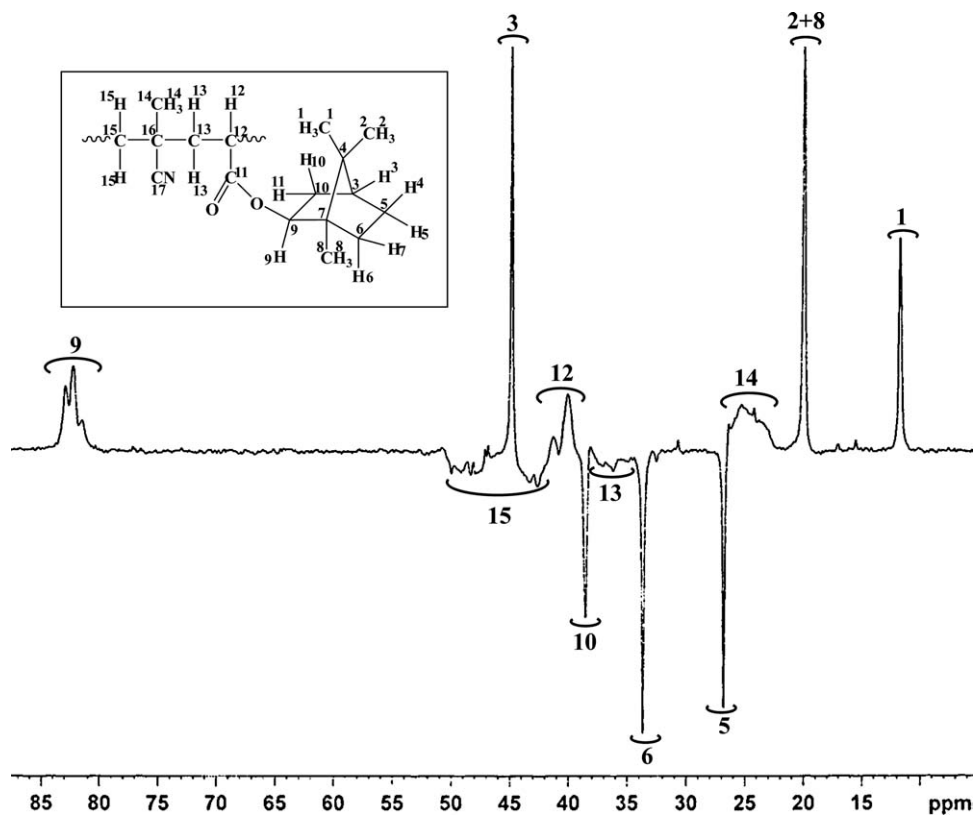


Figure 4 DEPT-135 NMR spectrum of the B/N copolymer ($F_B = 0.41$) in CDCl_3 at 25°C .

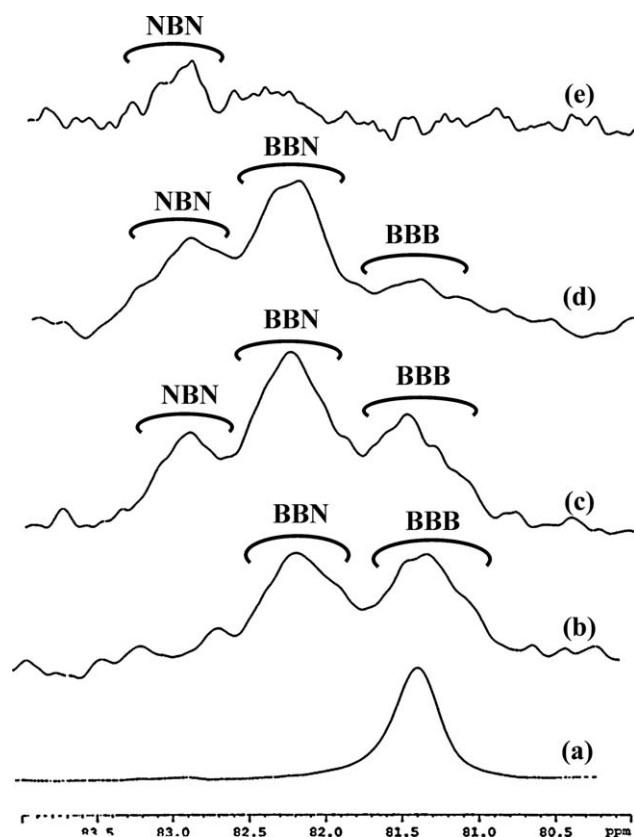


Figure 5 Expanded methine (OCH) region of the isobornyl ring in the $^{13}\text{C}(^1\text{H})$ -NMR spectrum of the (a) PiBA and B/N copolymers with different compositions: $F_B =$ (b) 0.72, (c) 0.41, (d) 0.30, and (e) 0.21 in CDCl_3 at 25°C .

Reactivity ratio determination

The composition of the different B/N copolymers were determined with the help of quantitative $^{13}\text{C}(^1\text{H})$ -NMR spectroscopy [Fig. 3(a)]. The quantitative $^{13}\text{C}(^1\text{H})$ -NMR experiments were carried out with an inverse-gated decoupling pulse program with 12 s delay time. The intensities of the carbonyl carbon of the B unit and the nitrile carbon of the N unit were used to determine the compositions of the B/N copolymers. Table I shows the comonomer molar fraction in the feed and in the copolymers. The copolymer composition data were used to determine the reactivity ratios of the comonomers with the KT²³ method. The reactivity ratios from EVM²⁴ were calculated with reactivity ratios obtained from the KT method along with the copolymer composition data. The reactivity ratios of the comonomers in the B/N copolymer obtained from the KT and EVM methods were as follows: $r_B = 0.66 \pm 0.11$ and $r_N = 1.54 \pm 0.22$ and $r_B = 0.74$ and $r_N = 1.65$, respectively. The values of the reactivity ratios of the B/N copolymers have not been reported in the literature.

RESULTS AND DISCUSSION

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

The completely assigned $^{13}\text{C}(^1\text{H})$ -NMR spectrum of the B/N copolymer ($F_B = 0.41$) in CDCl_3 at room temperature (25°C) is shown in Figure 3(a). The spectrum of the copolymer was quite complex and overlapped. The various resonance signals in the copolymers were assigned on the basis of a comparison with the spectra of PMAN²⁷ and poly(isobornyl acrylate) (PiBA).²⁸ The spectrum was further resolved with the help of the DEPT-135 NMR spectrum (Fig. 4), in which methine and methyl carbon appeared as a positive signal and the methylene carbon appeared as a negative signal.

The signals at δ values of 11.8 and 19.9 were assigned to methyl carbons (C_1 and C_2+C_8) of the B unit, respectively in the B/N copolymer. The region around δ values of 22.3–29.5 was assigned to the overlap of α -methyl carbon (C_{14}) of the N unit and methylene carbon (C_5) of isobornyl ring of the B unit in the B/N copolymer. The resonance signal of α -methyl carbon was well separated, spread over a wide range of chemical shifts, and assigned to a

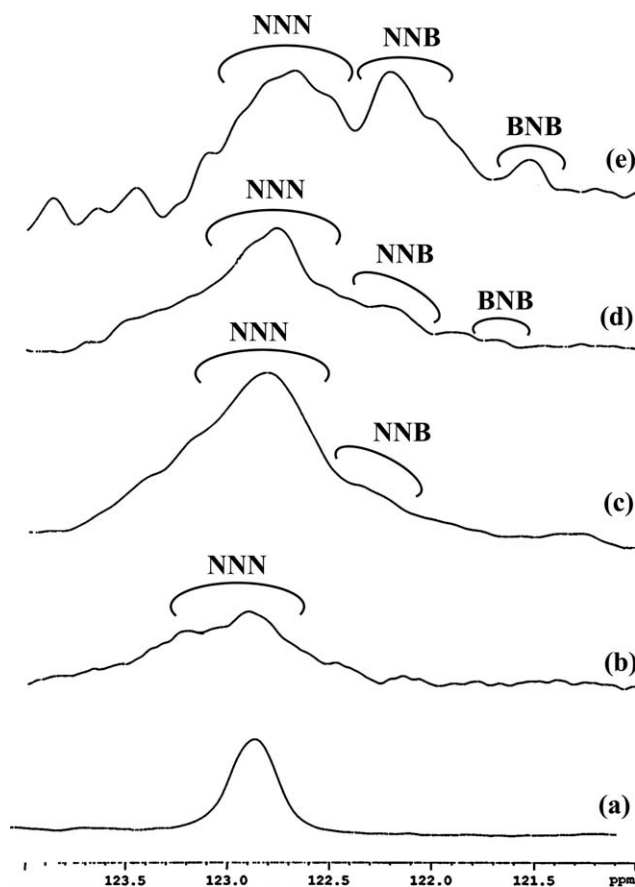


Figure 6 Expanded nitrile carbon region of the (a) PMAN and B/N copolymer with different compositions: $F_B =$ (b) 0.21, (c) 0.30, (d) 0.41, and (e) 0.72 in CDCl_3 at 25°C .

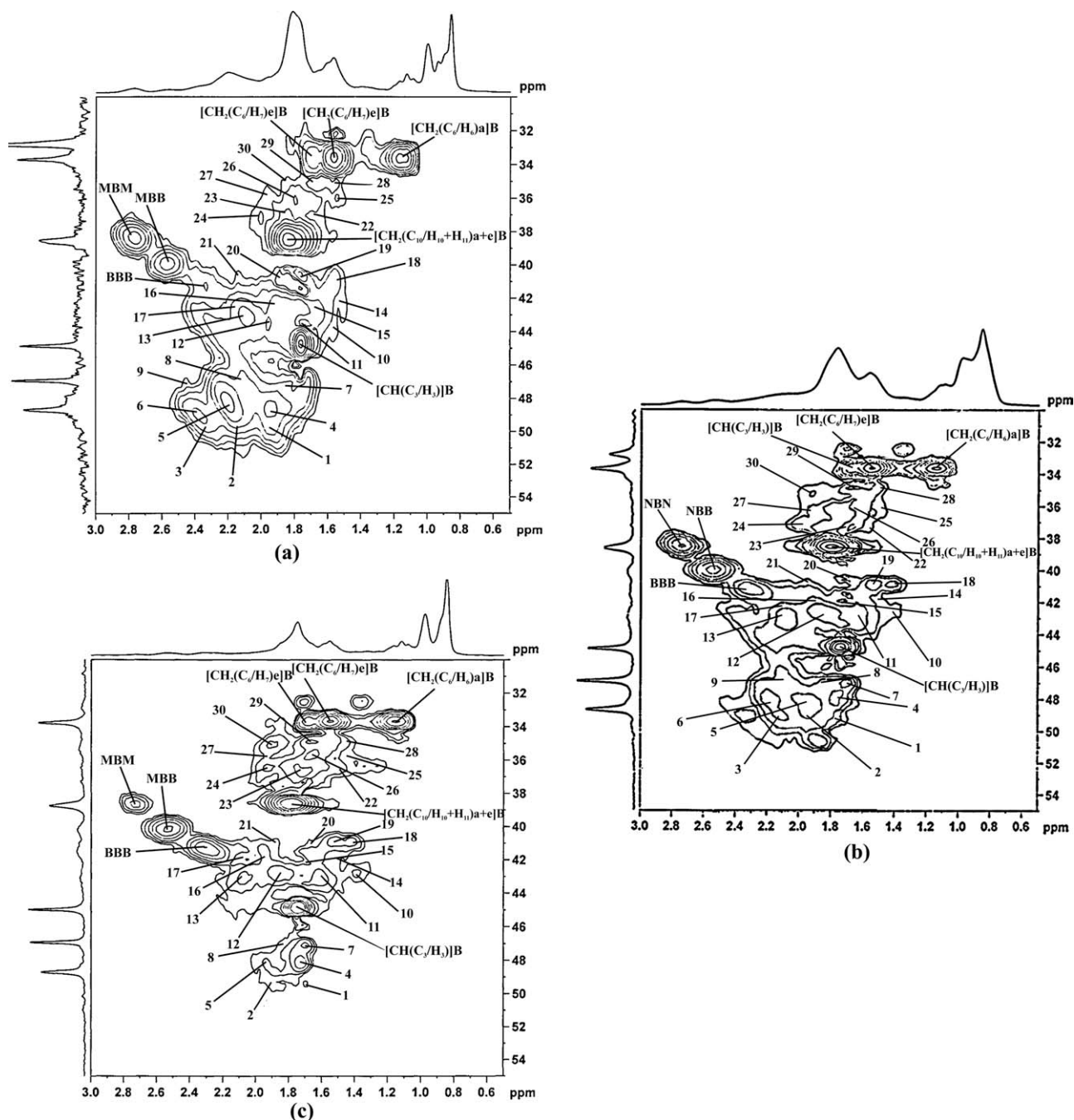


Figure 7 Expanded β -methylene and methine carbon regions of the 2D HSQC spectra of the B/N copolymers with different compositions: F_B = (a) 0.21, (b) 0.41, and (c) 0.72 in CDCl_3 at 25°C .

triad level of compositional and configurational sequences [Fig. 3(b)]. The resonance signals at δ values of 23.4 and 24.1 were assigned to NrNrN (r = racemic) and NrNmN (m = meso) triads of α -methyl carbon, respectively, whereas the resonance signal at a δ value of 25.4 was assigned to the overlap of NrNrB and NmNmN triads of α -methyl carbon. The resonance signal at a δ value of 26.8 was assigned to the overlap of NrNmB and BrNrB triads of α -methyl carbon along with methylene carbon (C_5) of the B unit, whereas the signal around a δ value of 28.7

was assigned to BrNmB triad of α -methyl carbon. These assignments were further confirmed by 2D HSQC spectra.

The expanded β -methylene carbon region of the B and N units of the B/N copolymers were sensitive up to tetrad level of compositional and configurational sequences. The overlapped resonance signals around δ values of 41.5–49.7 were assigned to β -methylene carbon (C_{15}) of the N unit and methine carbon (C_3) of the B unit in the B/N copolymer. This resonance signal was further resolved by DEPT-135

TABLE II
Assignment of the β -Methylene Carbon Resonance of the B/N Copolymers from the 2D HSQC Spectra

Sample	Cross-peak assignment	Peak position ($^1\text{H}/^{13}\text{C}$ δ)
1	NNmNN(H_a)	1.78/49.0
2	NNrNN	1.92/49.0
3	NNmNN(H_b)	2.15/49.0
4	BNmNN(H_a)	1.77/48.0
5	BNrNN	1.93/48.1
6	BNmNN(H_b)	2.18/48.0
7	BNmNB(H_a)	1.71/47.1
8	BNrNB	1.86/47.0
9	BNmNB(H_b)	2.10/47.0
10	NNmBN(H_a)	1.40/42.8
11	NNrBN(H_a)	1.61/42.9
12	NNrBN(H_b)	1.83/43.0
13	NNmBN(H_b)	2.08/43.0
14	BNmBN/NNmBB(H_a)	1.50/41.9
15	BNrBN/NNrBB(H_a)	1.69/42.0
16	BNrBN/NNrBB(H_b)	1.90/42.1
17	BNmBN/NNmBB(H_b)	2.08/42.1
18	BNmBB(H_a)	1.41/40.9
19	BNrBB(H_a)	1.52/40.9
20	BNrBB(H_b)	1.70/40.8
21	BNmBB(H_b)	1.91/41.0
22	NBmBN(H_a)	1.49/37.1
23	NBrBN	1.70/37.1
24	NBmBN(H_b)	1.93/37.1
25	NBmBB(H_a)	1.44/36.0
26	NBrBB	1.63/36.0
27	NBmBB(H_b)	1.90/36.0
28	BBmBB(H_a)	1.48/34.9
29	BBrBB	1.68/34.9
30	BBmBB(H_b)	1.93/35.0

NMR spectroscopy, as shown in Figure 4. The broad signal around δ values of 38.2–41.1 was assigned to methine carbon (C_{12}) of the B unit in the B/N copolymer. The broad signal around δ values of 34.5–37.2 was assigned to β -methylene carbon (C_{13}) of B unit. The methylene carbon (C_{10}) of isobornyl ring of the B unit gave a signal at a δ value of 38.4. The quaternary carbons (C_4 and C_7) gave resonances at δ values of 47.57 and 49.33, respectively, which did not appear in the DEPT-135 spectrum. The resonance peaks around δ values of 32.5–34.0 were assigned to the overlap of methylene carbon (C_6) of the isobornyl ring of the B unit and quaternary carbon (C_{16}) of the N unit and disappeared in DEPT-135 NMR spectrum. The broad resonance signal around δ values of 172.5–174.0 was assigned to carbonyl carbon (C_{11}) of the B unit.

The splitting pattern of the OCH carbon (C_9) of isobornyl ring of the B unit was well separated, spread over a wide range of chemical shifts, and assigned to triad compositional sequences. The assignments were carried out by a comparison of the spectrum of the copolymer with that of PiBA and by observations of the changes in the intensity of signals with changes in the composition of the

copolymers. The resonance signals around δ values of 81.42, 82.23, and 82.84 were assigned to the BBB, BBN, and NBN triads, respectively, as shown in Figure 5. Similarly, the resonance signal of nitrile carbon (C_{17}) of the N unit was spread over a wide range of chemical shifts, and the assignments were carried out by observation of the changes in the intensity of signals with changes in the composition of the copolymers and by comparison with the spectrum of PMAN. The resonance signals around δ values of 122.83, 122.19, and 121.52 were assigned to NNN, NNB, and BNB compositional triads, respectively, as shown in Figure 6.

2D HSQC and TOCSY NMR studies

The broad and overlapped resonance signals of the ^1H -NMR spectrum (Fig. 2) could not be assigned by 1D (^1H -NMR) spectral analysis and was assigned completely by a one-to-one correlation between the carbon and proton signals in the 2D HSQC spectrum. The assignments carried out by HSQC spectroscopy were further confirmed by 2D TOCSY experiment. 2D TOCSY was used to confirm the geminal couplings between nonequivalent protons of the same methylene group.

β -Methylene carbon resonances

The racemic methylene protons of the BrB- and NrN-centered tetrads were in the same environment and resulted a single cross-peak in 2D HSQC spectrum. Two nonequivalent methylene mesoprotons (H_a and H_b) of the BB- and NN-centered tetrads gave two cross-peaks in the 2D HSQC spectrum and one cross-correlation peak in the 2D TOCSY spectrum, so the 2D TOCSY spectrum could differentiate between the meso and racemic protons and confirmed the 2D HSQC assignments.

The expanded β -methylene region in 2D HSQC spectra is given in Figure 7, and the assignments are listed in Table II. All of the assignments were carried out on the basis of a comparison with the spectra of PMAN²⁷ and PiBA.²⁸ The cross-peaks 1 and 3 were assigned to NNmNN(H_a) and NNmNN(H_b) tetrads, respectively, whereas NNrNN tetrad was assigned to the cross-peak 2. The BNNN and BNNB tetrads of the copolymer were assigned by observing the changes in intensities of the cross-peaks with changes in the copolymer composition. BNmNN(H_a) and BNmNN(H_b) gave rise to two cross-peaks, 4 and 6, whereas BNrNN tetrad was assigned to cross-peak 5. On the basis of variation in the intensity of signals with the copolymer composition, the cross-peaks 7, 9, and 8 were assigned to BNmNB(H_a), BNmNB(H_b), and BNrNB tetrads, respectively. The H_a and H_b

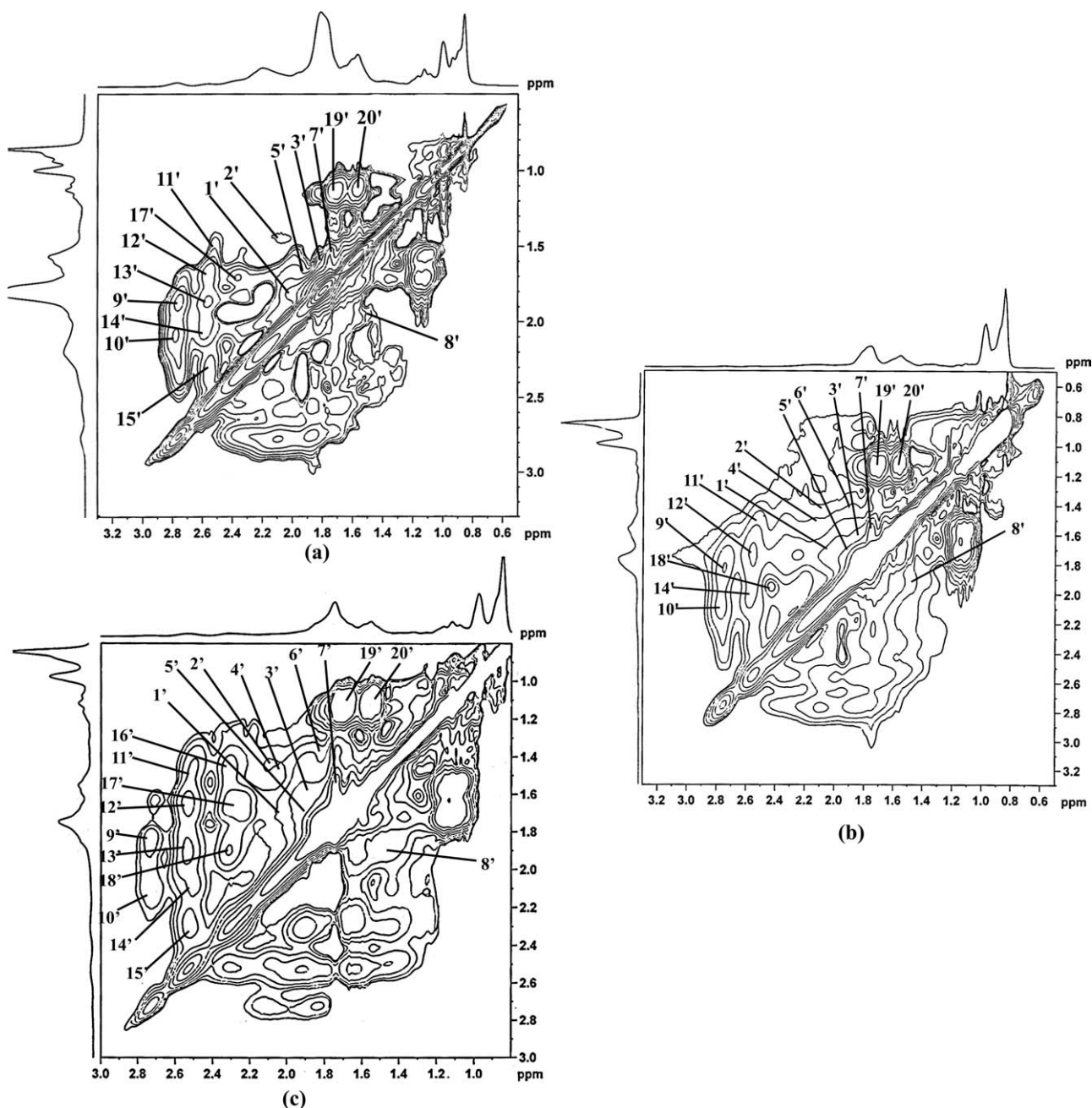


Figure 8 Expanded 2D TOCSY spectra of the B/N copolymers with different compositions: $F_B =$ (a) 0.21, (b) 0.41, and (c) 0.72 in CDCl_3 at 25°C .

protons of NNmNN, BNmNN, and BNmNB tetrads coupled together to give the cross-correlation peak 1' in the 2D TOCSY spectrum (Fig. 8). The methylene protons H_a and H_b of both NmB- and NrB-centered tetrads were in a different magnetic environment and, thus, resulted in two cross-peaks by coupling with methylene carbon in the 2D HSQC spectrum. Because H_a and H_b of NmB and NrB were nonequivalent, they also gave a cross-correlation peak in the 2D TOCSY spectrum; this enabled to differentiate between the cross-peaks of both NmB and NrB in the 2D HSQC spectrum.

The NNmBN(H_a) and NNmBN(H_b) tetrads were assigned to cross-peaks 10 and 13, whereas NNrBN(H_a) and NNrBN(H_b) tetrads were assigned to cross-peaks 11 and 12, respectively, as shown in Figure 7. The H_a and H_b protons of NNmBN and NNrBN tetrads coupled together and gave cross-correlation peaks 2' and 3', respectively. The BNmBN/NNmBB(H_a), BNmBN/NNmBB(H_b), BNrBN/NNrBB(H_a), and BNrBN/NNrBB(H_b) tetrads were attributed to cross-peaks 14, 17, 15, and 16, respectively. Similarly, BNmBB(H_a), BNmBB(H_b), BNrBB(H_a), and BNrBB(H_b) were assigned to the

TABLE III
 ^1H - ^1H Cross-Correlation between the Nonequivalent Geminal Protons in the B/N Copolymers Observed from the 2D TOCSY Spectra

Correlation peak number	Coupled protons		Peak position 2D TOCSY ($^1\text{H}/^1\text{H}$, δ)
	Proton I	Proton II	
1'	CH_2 of $\text{NNmNN}(\text{H}_a) + \text{CH}_2$ of $\text{BNmNN}(\text{H}_a) + \text{CH}_2$ of $\text{BNmNB}(\text{H}_a)$	CH_2 of $\text{NNmNN}(\text{H}_b) + \text{CH}_2$ of $\text{BNmNN}(\text{H}_b) + \text{CH}_2$ of $\text{BNmNB}(\text{H}_b)$	1.75/2.13
2'	CH_2 of $\text{NNmBN}(\text{H}_a)$	CH_2 of $\text{NNmBN}(\text{H}_b)$	1.40/2.08
3'	CH_2 of $\text{NNrBN}(\text{H}_a)$	CH_2 of $\text{NNrBN}(\text{H}_b)$	1.61/1.83
4'	CH_2 of $\text{BNmBN}/\text{NNmBB}(\text{H}_a)$	CH_2 of $\text{BNmBN}/\text{NNmBB}(\text{H}_b)$	1.50/2.08
5'	CH_2 of $\text{BNrBN}/\text{NNrBB}(\text{H}_a)$	CH_2 of $\text{BNrBN}/\text{NNrBB}(\text{H}_b)$	1.69/1.90
6'	CH_2 of $\text{BNmBB}(\text{H}_a)$	CH_2 of $\text{BNmBB}(\text{H}_b)$	1.41/1.91
7'	CH_2 of $\text{BNrBB}(\text{H}_a)$	CH_2 of $\text{BNrBB}(\text{H}_b)$	1.52/1.70
8'	CH_2 of $\text{NBmBN}(\text{H}_a) + \text{CH}_2$ of $\text{NBmBB}(\text{H}_a) + \text{CH}_2$ of $\text{BBmBB}(\text{H}_a)$	CH_2 of $\text{NBmBN}(\text{H}_b) + \text{CH}_2$ of $\text{NBmBB}(\text{H}_b) + \text{CH}_2$ of $\text{BBmBB}(\text{H}_b)$	1.46/1.91
9'	CH_2 of $\text{NrB}(\text{H}_b)$	CH of NBN	1.84/2.75
10'	CH_2 of $\text{NmB}(\text{H}_b)$	CH of NBN	2.11/2.75
11'	CH_2 of $\text{BmB}(\text{H}_a)$	CH of BBN	1.46/2.51
12'	CH_2 of $\text{BrB} + \text{CH}_2$ of $\text{NrB}(\text{H}_a)$	CH of BBN	1.67/2.51
13'	CH_2 of $\text{BmB}(\text{H}_b) + \text{CH}_2$ of $\text{NmB}(\text{H}_b)$	CH of BBN	1.90/2.51
14'	CH_2 of $\text{NmB}(\text{H}_b)$	CH of BBN	2.09/2.51
15'	CH of BBB	CH of BBN	2.3/2.51
16'	CH_2 of $\text{BmB}(\text{H}_a)$	CH of BBB	1.44/2.31
17'	CH_2 of BrB	CH of BBB	1.68/2.31
18'	CH_2 of $\text{BmB}(\text{H}_b)$	CH of BBB	1.90/2.31
19'	$\text{CH}_2(\text{H}_6)_a$ of B	$\text{CH}_2(\text{H}_5)_c$ of B	1.11/1.72
20'	$\text{CH}_2(\text{H}_4$ and $\text{H}_6)_a$ of B	$\text{CH}_2(\text{H}_7)_e$ of B	1.11/1.55

cross-peaks 18, 21, 19, and 20, respectively. The H_a and H_b protons of $\text{BNmBN}/\text{NNmBB}$, $\text{BNrBN}/\text{NNrBB}$, BNmBB , and BNrBB tetrads coupled to give the cross-correlation peaks 4', 5', 6', and 7', respectively, in the 2D TOCSY spectrum (Table III). The BB -centered tetrads also showed compositional and configurational sensitivity. The $\text{NBmBN}(\text{H}_a)$, NBrBN , and $\text{NBmBN}(\text{H}_b)$ tetrads gave the cross-peaks 22, 23, and 24, respectively, whereas $\text{NBmBB}(\text{H}_a)$, NBrBB , and $\text{NBmBB}(\text{H}_b)$ tetrads showed the cross-peaks 25, 26, and 27, respectively. The BBBB tetrad was assigned by comparison with the 2D HSQC and TOCSY spectra of PiBA. $\text{BBmBB}(\text{H}_a)$ and $\text{BBmBB}(\text{H}_b)$ were assigned to the cross-peaks 28 and 30, respectively, whereas cross-peak 29 was assigned to the BBBrBB tetrad. Geminal coupling between the H_a and H_b protons of NBmBN , NBmBB , and BBmBB tetrads were assigned to the cross-correlation peak 8' in the 2D TOCSY spectrum (Fig. 8).

Methine carbon resonances

The DEPT-135 NMR spectrum of the backbone methine carbon region is shown in Figure 4. The splitting pattern of the methine carbon was well separated and spread over a wide range of chemical shifts. The methine group of the B unit was assigned to the triad level of compositional sequences in the copolymers. The cross-peaks at $^{13}\text{C}/^1\text{H}$ δ values of 41.3/2.32, 40.2/2.53, and 38.4/2.75 were assigned to

BBB , BBN , and NBN triads, respectively, as shown in Figure 7. We used 2D TOCSY studies to confirm these assignments by assigning the 1,3 bond couplings between methine and methylene protons of the B unit in BB -, NB -, and NN -centered tetrads. The cross-correlation peak 9' was assigned to the coupling of NBN triad with methylene protons of the $\text{NrB}(\text{H}_b)$ tetrads, and the cross-correlation peak 10' was due to the coupling of NBN triad with the methylene protons of $\text{NmB}(\text{H}_b)$ tetrad (Table III). The methine proton of NBB triad showed a cross-correlation with the methylene protons of $\text{BmB}(\text{H}_a)$, $\text{BrB} + \text{NrB}(\text{H}_a)$, $\text{BmB}(\text{H}_b) + \text{NmB}(\text{H}_b)$, and $\text{NmB}(\text{H}_b)$ dyads and gave cross-correlation peaks 11', 12', 13', and 14', respectively. The methine proton of NBB triad also showed 1,4 bond coupling with the methine proton of BBB triad and gave the cross-correlation peak 15'. The cross-correlation peaks 16', 17', and 18', as shown in Figure 8, were assigned to the coupling of BBB triad of the methine proton with the methylene protons of $\text{BmB}(\text{H}_a)$, BrB , and $\text{BmB}(\text{H}_b)$ tetrads, respectively. The cross-correlation peaks 19' and 20' were assigned to the coupling of the axial methylene proton ($\text{H}_4 + \text{H}_6$) with equatorial methylene protons (H_5 and H_7) of the B unit, respectively. All of the TOCSY assignments are shown in Table III.

α -Methyl carbon resonances

The expanded α -methyl region of the 2D HSQC-NMR spectra of the B/N copolymers are shown in

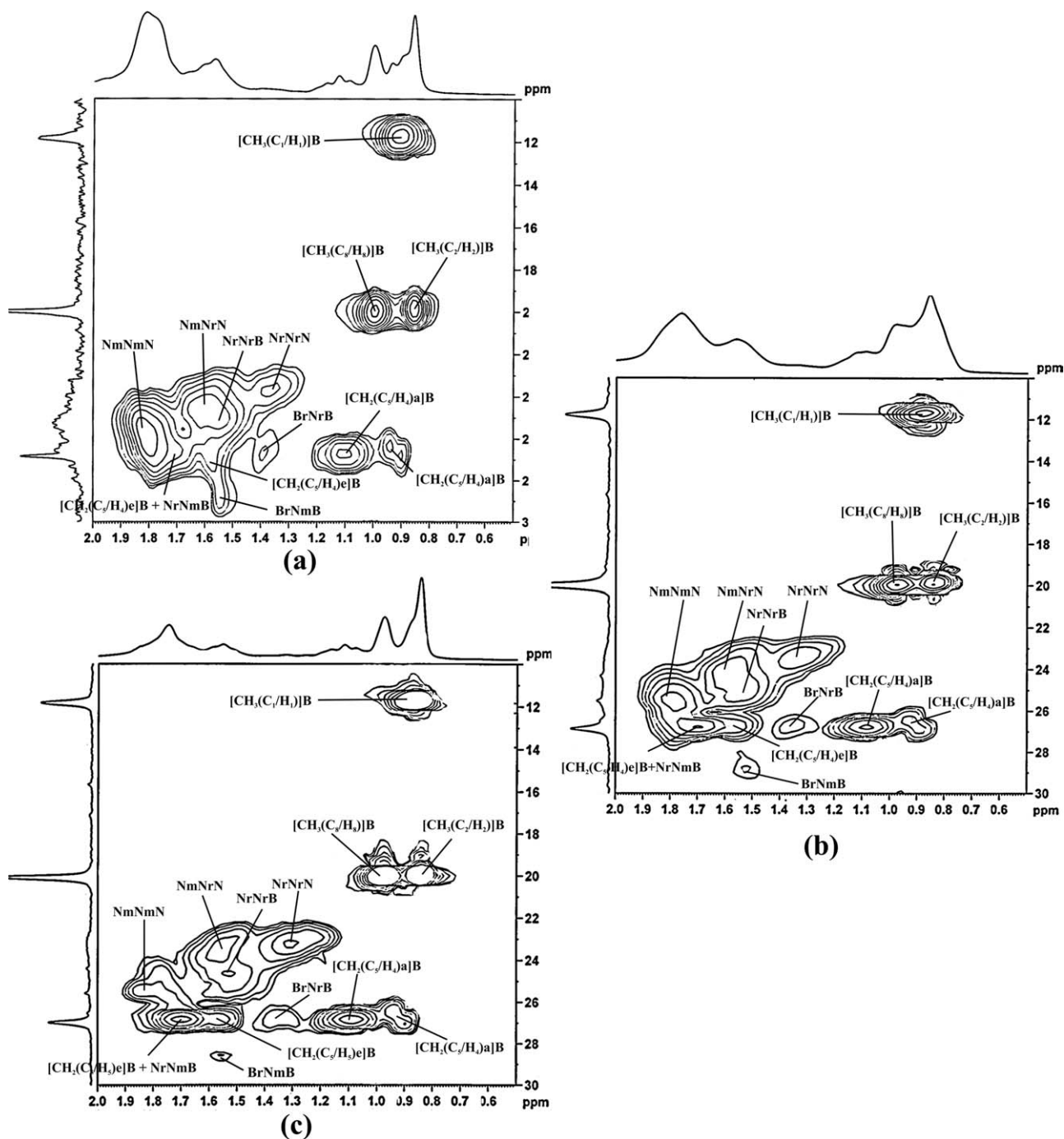


Figure 9 Expanded α -methyl carbon regions of the 2D HSQC spectra of the B/N copolymers with different compositions: $F_B =$ (a) 0.21, (b) 0.41, and (c) 0.72 in CDCl_3 at 25°C .

Figure 9 [(a) $F_B = 0.21$, (b) $F_B = 0.41$, and (c) $F_B = 0.72$]. The α -CH₃ region of the N unit in the copolymer showed compositional and configurational sensitivity. The cross-peaks at $^{13}\text{C}/^1\text{H}$ δ values of 23.5/1.34, 23.9/1.58, and 25.7/1.79 were assigned to NrNrN, NrNmN, and NmNmN triads, respectively. The cross-peaks at δ values of 25.1/1.55, 26.7/1.70, and δ 26.9/1.38 were assigned to NrNrB, NrNmB + [CH₂(C₅/H₄)e]B, and BrNrB triads, respectively, whereas the cross-peak at a δ value of 28.8/1.54 was

assigned to BrNmB triad of the α -methyl carbon, as shown in Figure 9.

2D HMBC studies

2D HMBC spectroscopy can be used to study long-range couplings between proton and carbon nuclei. Neither the nitrile or quaternary carbons showed any coupling in the 2D HSQC spectrum. To investigate the compositional and configurational

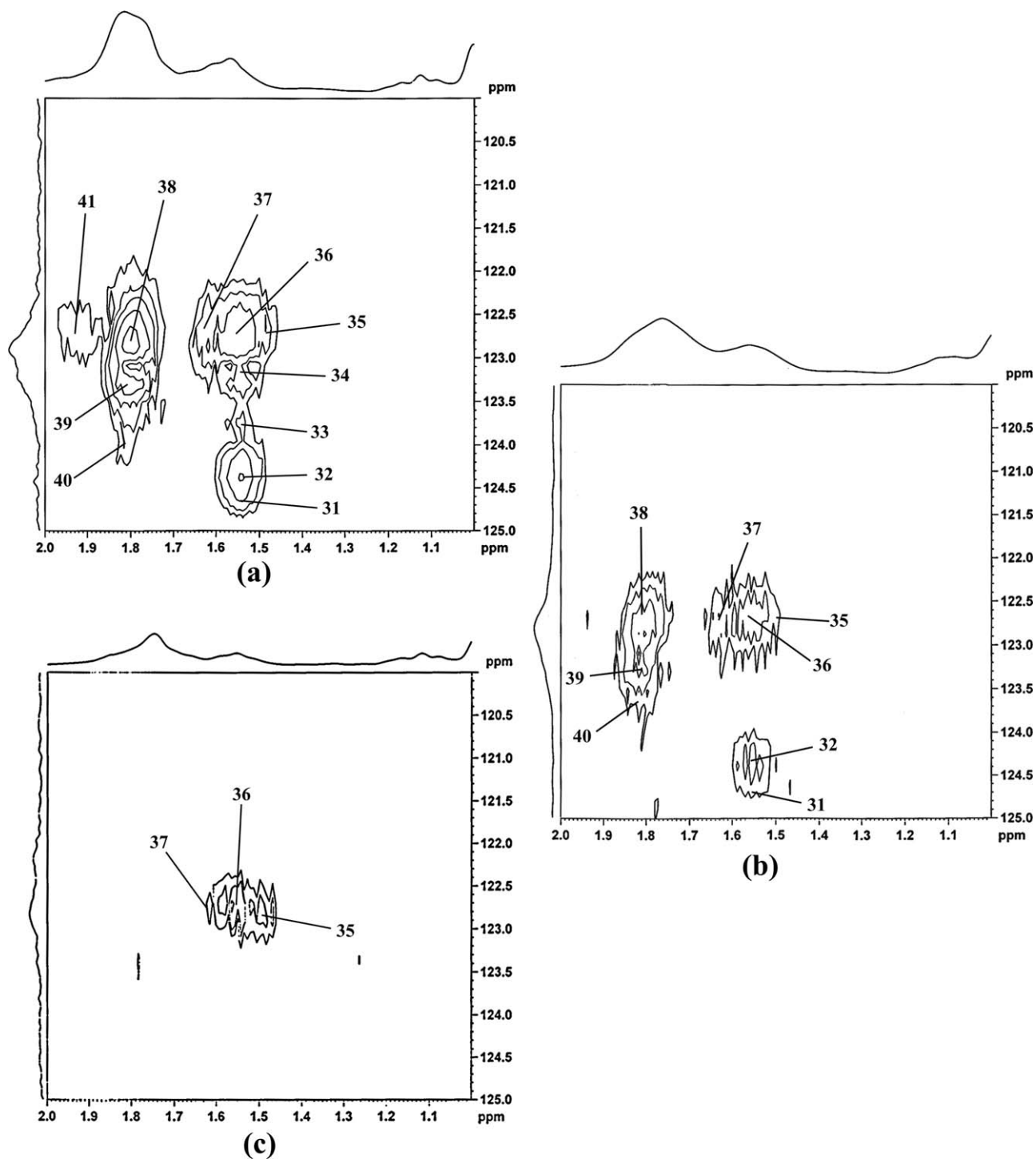


Figure 10 Expanded 2D HMBC spectra of the B/N copolymers of the nitrile region with different compositions: $F_B =$ (a) 0.21, (b) 0.41, and (c) 0.72 in CDCl_3 at 25°C .

sensitivities of these carbon resonances, the 2D HMBC spectra of different copolymer compositions were recorded, wherein we could see the long-range couplings of nitrile and quaternary carbon resonances with the methylene, methine, and methyl protons. The methylene protons were assigned to tetrad level with the 2D HSQC spectra; this was confirmed

by 2D TOCSY studies, which enabled to assign the quaternary and nitrile carbon resonances.

Nitrile carbon resonances

The 2D HMBC spectra showing the nitrile carbon couplings with α -methyl and β -methylene protons

TABLE IV
Coupling of the Nitrile Carbon with the α -Methyl and β -Methylene Protons of the B/N Copolymers on the Basis of the 2D HMBC Spectra

Cross-peak number	Peak position ($^{13}\text{C}/^1\text{H}$ δ)	Type of carbon	Coupled to the proton of
31	124.72/1.55	CN(NrNrN)	α -CH ₃ of NNN
32	124.36/1.55	CN(NmNrN)	α -CH ₃ of NNN
33	123.77/1.55	CN(NmNmN)	α -CH ₃ of NNN
34	123.28/1.55	CN(NNB)	β -CH ₂ of [NmB(H _a)]
35	122.65/1.48	CN(BNB)	β -CH ₂ of [NmB(H _a)]
36	122.65/1.55	CN(BNB)	α -CH ₃ of BNB
37	122.65/1.62	CN(BNB)	β -CH ₂ of [NrB(H _a)]
38	122.79/1.81	CN(BNB)	β -CH ₂ of [NrB(H _b)]
39	123.30/1.81	CN(NNB)	β -CH ₂ of [NmN(H _a)] + β -CH ₂ of [NrB(H _b)]
40	124.20/1.81	CN(NmNrN)	β -CH ₂ of [NmN(H _a)]
41	122.61/1.92	CN(BNB)	β -CH ₂ of [NmB(H _b)]

are given in Figure 10. To assign nitrile carbon resonances in the B/N copolymer, the analysis of couplings between the α -methyl and β -methylene protons with nitrile carbon was taken into consideration. The α -methyl protons of NNN triad were coupled with the nitrile carbon of NrNrN triad and gave the cross-peak 31. The cross-peaks 32 and 33 were assigned to the coupling of NrNmN and NmNmN triads of the nitrile carbon with NNN triad of the α -methyl protons, respectively. The NNB and BNB triads of the nitrile carbon were coupled with NmB(H_a) dyad of the β -methylene protons and gave the cross-peaks 34 and 35, respectively. The BNB triad of the nitrile carbon were coupled with the same triad of the α -methyl protons and gave cross-peak 36. The NrB(H_a) and NrB(H_b) dyads of the β -methylene protons were coupled with BNB triad of the nitrile carbons and gave the cross-peaks 37 and 38, respectively. Cross-peak 39 was assigned to the coupling of NNB triad of the nitrile carbon with the β -methylene proton of NmN(H_a) + NrB(H_b) dyad. The NmNrN triad of the nitrile carbon was coupled with NmN(H_a) dyad of the β -methylene protons and gave the cross-peak 40, whereas cross-peak 41 was assigned to the coupling of BNB triad of the nitrile carbon with NmB(H_b) dyad of β -methylene proton. All of the assignments are listed in Table IV.

Quaternary and other aliphatic carbon resonances

The 2D HMBC spectrum showing the quaternary and other aliphatic carbon couplings with the methyl, methylene, and methine protons are given in Figure 11. Cross-peaks 42 and 43 were assigned to the interaction of the methyl carbon (C₁) with the methyl protons (H₂) and methylene proton (H₄), respectively. Cross-peaks 44, 45, and 46 were assigned to the coupling of the methyl carbons (C₂ + C₈) with the methyl protons (H₁) and methylene protons (H₄ and H₆), respectively. The methylene

carbon (C₅) showed interaction with the methyl protons (H₁ + H₂), methylene protons (H₄), and methyl protons (H₈) and gave cross-peaks 47, 48, and 49, respectively. Cross-peak 50 was assigned to the coupling of the methylene carbon (C₆) with the methyl protons (H₁ + H₂). Cross-peaks 51 and 52 were assigned to the coupling of the methine carbon (C₃) with the methyl protons (H₁ + H₂ and H₈, respectively). The quaternary carbon (C₄) showed interaction with the methyl protons (H₁ + H₂ and H₈), methylene proton (H₄), and methine proton (H₃) and gave the cross-peaks 53, 54, 57, and 59, respectively. The quaternary carbon (C₇) gave cross-peaks 55, 56, and 58 on coupling with the methyl protons (H₁ + H₂ and H₈) and methylene proton (H₅), respectively. The methine carbon (C₃) showed interaction with the methylene protons (H₁₀ + H₁₁) and gave cross-peak 60. Cross-peak 61 was assigned to the interaction of the methylene carbon (C₅) with the methylene proton (H₆). Cross-peak 62 was assigned to the interaction of the quaternary carbon (C₄) with the OCH proton (H₉), whereas cross-peak 63 was assigned to the interaction of the OCH (C₉) carbon with the methyl protons (H₁ + H₂). Cross-peaks 64, 65, and 66 were assigned to the interaction of the methylene carbon (C₆) with the methylene proton (H₅), methine proton (H₃), and methylene protons (H₁₀ + H₁₁), respectively. All of the assignments are given in Table V.

$^1\text{H-NMR}$ studies

The overlapped $^1\text{H-NMR}$ spectrum of the B/N copolymer (Fig. 2) was completely assigned with the help of 2D HSQC, TOCSY, and $^1\text{H-NMR}$ spectra of PMAN and PiBA. The signal around a δ value of 4.62 was assigned to the OCH (H₉) proton, whereas the signal around δ values of 2.32–2.75 was assigned to CH (H₁₂) proton of the B unit. The signals around δ values of 1.52–1.72 and 0.92–1.08

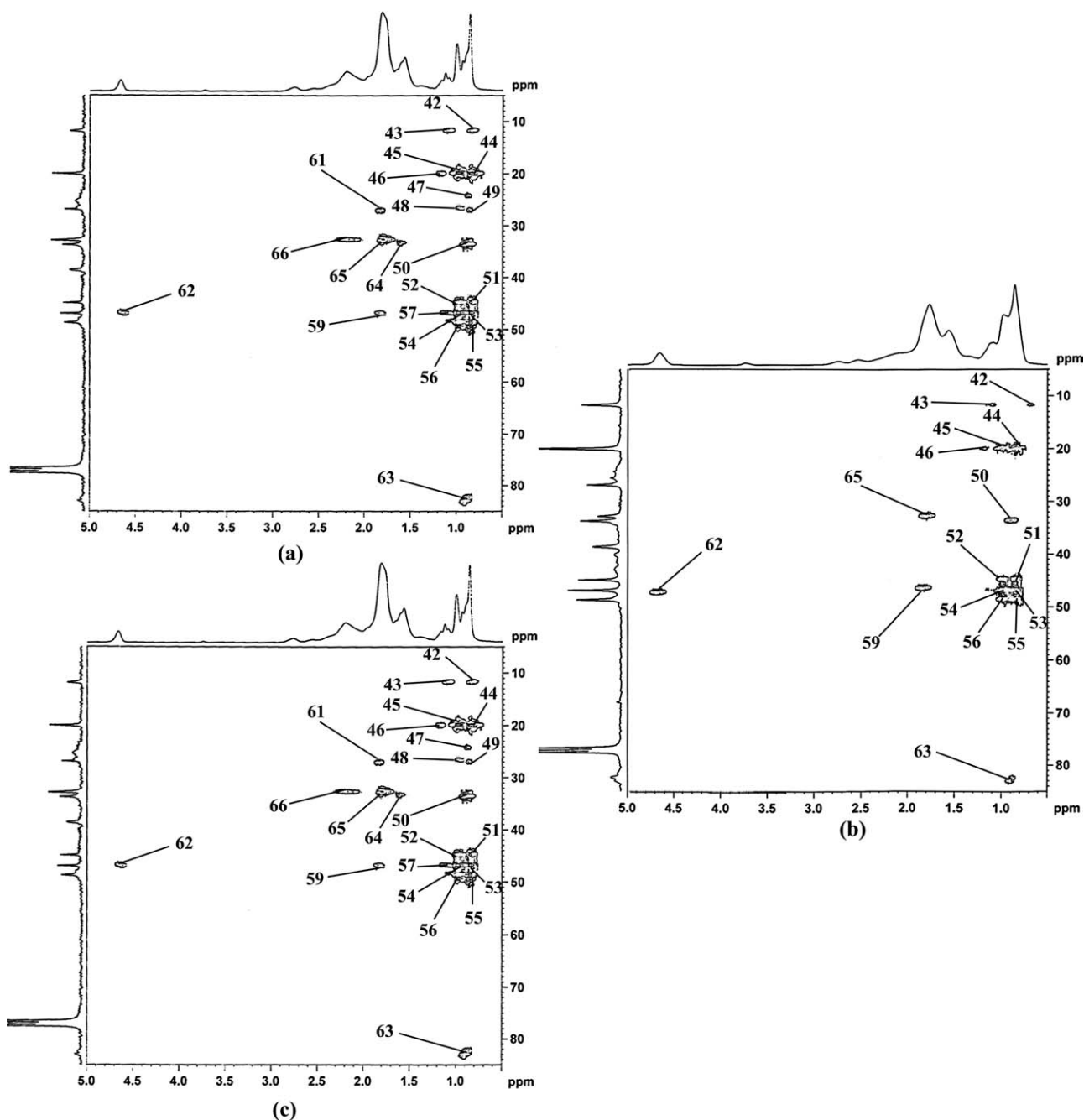


Figure 11 Expanded 2D HMBC spectra of the B/N copolymers of the aliphatic region with different compositions: $F_B =$ (a) 0.21, (b) 0.41, and (c) 0.72 in CDCl_3 at 25°C .

were assigned to the equatorial methylene protons (H_5 and H_7) and the axial methylene protons (H_4 and H_6) of isobornyl ring of the B unit, respectively. The signal around δ values of 1.64–1.92 was assigned to isobornyl ring protons (H_3 , H_{10} , and H_{11}) of the B unit, whereas the signal around δ values of 1.41–2.18 was assigned to β -methylene protons (H_{13} and H_{15}) of the B/N copolymer. The α -methyl protons (H_{14}) of the N unit gave their signal around δ values of 1.34–1.82. The signals at δ values of 0.88 and 0.95 were assigned to the methyl protons

(H_1 , H_2 and H_8) of isobornyl ring of the B unit, respectively.

CONCLUSIONS

The reactivity ratios of the comonomers in the B/N copolymer determined from the linear KT method and nonlinear EVM were $r_B = 0.66 \pm 0.11$ and $r_N = 1.54 \pm 0.22$ and $r_B = 0.74$ and $r_N = 1.65$, respectively. The complex and overlapped $^1\text{H-NMR}$ and

TABLE V
2D HMBC Assignments of the Quaternary and Other Aliphatic Carbon Resonances of the B/N Copolymers

Cross-peak number	Peak position ($^{13}\text{C}/^1\text{H}$, δ)	Type of carbon	Coupled to proton of
42	12.0/0.88	$\text{CH}_3(\text{C}_1)$	$\text{CH}_3(\text{H}_2)$
43	12.0/1.02	$\text{CH}_3(\text{C}_1)$	$\text{CH}_2(\text{C}_4)$
44	20.20/0.88	$\text{CH}_3(\text{C}_2 + \text{C}_8)$	$\text{CH}_3(\text{H}_1)$
45	20.20/1.02	$\text{CH}_3(\text{C}_2 + \text{C}_8)$	$\text{CH}_2(\text{H}_4)$
46	20.20/1.20	$\text{CH}_3(\text{C}_2 + \text{C}_8)$	$\text{CH}_2(\text{H}_6)$
47	24.5/0.90	$\text{CH}_2(\text{C}_5)$	$\text{CH}_3(\text{H}_1 + \text{H}_2)$
48	26.5/1.00	$\text{CH}_2(\text{C}_5)$	$\text{CH}_2(\text{H}_4)$
49	27.0/0.95	$\text{CH}_2(\text{C}_5)$	$\text{CH}_3(\text{H}_8)$
50	34.0/0.88	$\text{CH}_2(\text{C}_6)$	$\text{CH}_3(\text{H}_1 + \text{H}_2)$
51	45.0/0.88	$\text{CH}(\text{C}_3)$	$\text{CH}_3(\text{H}_1 + \text{H}_2)$
52	45.0/0.95	$\text{CH}(\text{C}_3)$	$\text{CH}_3(\text{H}_8)$
53	47.0/0.88	$\text{C}(\text{C}_4)$	$\text{CH}_3(\text{H}_1 + \text{H}_2)$
54	47.0/0.95	$\text{C}(\text{C}_4)$	$\text{CH}_3(\text{H}_8)$
55	49.0/0.88	$\text{C}(\text{C}_7)$	$\text{CH}_3(\text{H}_1 + \text{H}_2)$
56	49.0/0.95	$\text{C}(\text{C}_7)$	$\text{CH}_3(\text{H}_8)$
57	47.0/1.05	$\text{C}(\text{C}_4)$	$\text{CH}_2(\text{H}_4)$
58	49.0/1.72	$\text{C}(\text{C}_7)$	$\text{CH}_2(\text{H}_5)$
59	47.0/1.80	$\text{C}(\text{C}_4)$	$\text{CH}(\text{H}_3)$
60	45.5/1.80	$\text{CH}(\text{C}_3)$	$\text{CH}_2(\text{H}_{10} + \text{H}_{11})$
61	27.0/1.08	$\text{CH}_2(\text{C}_5)$	$\text{CH}_2(\text{H}_6)$
62	47.0/4.62	$\text{C}(\text{C}_4)$	$\text{OCH}(\text{H}_9)$
63	81.9/0.88	$\text{OCH}(\text{C}_9)$	$\text{CH}_3(\text{H}_1 + \text{H}_2)$
64	34.4/1.60	$\text{CH}_2(\text{C}_6)$	$\text{CH}_2(\text{H}_5)$
65	33.4/1.80	$\text{CH}_2(\text{C}_6)$	$\text{CH}(\text{H}_3)$
66	33.4/1.90	$\text{CH}_2(\text{C}_6)$	$\text{CH}_2(\text{H}_{10} + \text{H}_{11})$

$^{13}\text{C}(^1\text{H})$ -NMR spectra of the B/N copolymers were resolved completely with the help of DEPT and 2D HSQC spectra. The nitrile carbon of the N unit and OCH carbon (C_9) of the B unit were assigned to triad compositional sequences in the $^{13}\text{C}(^1\text{H})$ -NMR spectrum. The α -methyl carbon of the N unit was assigned to triad compositional and configurational sequences and was further confirmed by 2D HSQC-NMR spectrum, whereas the β -methylene carbon resonances were assigned to tetrad compositional and configurational sequences. The methine carbon of the B unit was assigned to triad levels of compositional sequences. Geminal couplings within various β -methylene protons were observed in the 2D TOCSY spectrum. The long-range interactions of the quaternary and nitrile carbons with the methyl, methylene, and methine protons were completely assigned in the 2D HMBC spectrum.

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