

# Investigation of Microstructure of the Acrylonitrile-Styrene-Glycidyl Methacrylate Terpolymers by 1D and 2D NMR Spectroscopy

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**ABSTRACT:** Acrylonitrile-styrene-glycidyl methacrylate (N/S/G) terpolymers were prepared by bulk polymerization by using benzoyl peroxide as initiator and analyzed by NMR spectroscopy. The compositions of terpolymers were determined by quantitative  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra and compared with those calculated by Goldfinger's equation by using comonomer reactivity ratios:  $r_{\text{NS}} = 0.04$ ,  $r_{\text{SN}} = 0.40$ ;  $r_{\text{NG}} = 0.22$ ,  $r_{\text{GN}} = 1.37$ ;  $r_{\text{SG}} = 0.44$ ,  $r_{\text{GS}} = 0.53$ . The  $^{13}\text{C}\{^1\text{H}\}$ - and  $^1\text{H}$ -NMR spectra were overlapping and complex. The spectral assignments were done

with the help of distortionless enhancement by polarization transfer and two-dimensional  $^{13}\text{C}$ - $^1\text{H}$  heteronuclear single quantum correlation experiments. 2D total correlated spectroscopy was used to ascertain the various coupling between the protons. The methyl, methine, methylene, and oxymethylene carbon resonances showed compositional sensitivity. 2D nuclear Overhauser enhancement spectroscopy (NOESY) experiment was used to ascertain the spatial proton-proton couplings. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1779–1790, 2003

## INTRODUCTION

The growing interest in multicomponent polymerizations from both industry and academia has uncovered the need for a systematic approach to the study of such systems.<sup>1,2</sup> The aim of such a study is the understanding of the fundamental physicochemical phenomena and hence the production of improved chemical, physical, and mechanical properties that differ from those of the copolymers. However, the properties of a copolymer depend upon its microstructure.<sup>3</sup> The study of the microstructure of terpolymers requires prior knowledge about comonomer sequences in the copolymer system of the constituents.

High-resolution one-dimensional (1D) and two-dimensional (2D) NMR spectroscopy has proven to be one of the most informative techniques used for the investigation of polymer microstructures.<sup>4–11</sup> Acrylonitrile/styrene (N/S) is one of the widely studied copolymers.<sup>12–14</sup> Brar et al.<sup>15,16</sup> have reported the comonomer sequences and cotacticity in the acrylonitrile/glycidyl methacrylate (N/G) and styrene/glycidyl methacrylate (S/G) copolymers.

In this work, we report the monomer compositions obtained from quantitative  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra, the

compositional sequence distribution of the acrylonitrile/styrene/glycidyl methacrylate (N/S/G) terpolymer by 1D and 2D NMR spectroscopy. The  $^{13}\text{C}\{^1\text{H}\}$ - and  $^1\text{H}$ -NMR spectra of terpolymer are quite complex and have been interpreted with the help of distortionless enhancement by polarization transfer (DEPT) and 2D heteronuclear single quantum correlation (HSQC) NMR spectroscopy. 2D total correlated spectroscopy (TOCSY) NMR experiments are used to ascertain the various proton-proton couplings in the terpolymer chain. 2D NOESY experiment is used to ascertain the spatial coupling between the methylene protons and aromatic ring protons.

## EXPERIMENTAL

Acrylonitrile (E. Merck, Germany), styrene (G. S. Chemical, Bombay, India), and glycidyl methacrylate (E. Merck, Germany) monomers were vacuum distilled under reduced pressure and stored below 5°C. Acrylonitrile/styrene/glycidyl methacrylate (N/S/G) terpolymers were prepared by bulk polymerization at 60°C by using benzoyl peroxide as initiator. The percentage conversion was kept below 10% by precipitating the terpolymers in methanol. The terpolymers were purified by the chloroform/methanol system. The monomer compositions in the terpolymer were determined experimentally by quantitative  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy.

### NMR measurements

$^1\text{H}$ - and  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded in  $\text{CDCl}_3$  with a Bruker DPX 300 MHz spectrometer at a fre-

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TABLE I  
Terpolymer Compositions for Acrylonitrile-Styrene-Glycidyl Methacrylate Terpolymers (N/S/G)

Sample No.	Monomer	Feedmole fractions	Mole fractions in terpolymer		$\bar{M}_w^c \times 10^{-5}$ (g/mol)	$\bar{M}_n \times 10^{-5}$ (g/mol)	$\bar{P}^d$
			a	b			
1	N	0.18	0.14	0.13	4.40	3.04	1.45
	S	0.11	0.19	0.20			
	G	0.71	0.67	0.67			
2	N	0.16	0.25	0.22	3.73	2.40	1.55
	S	0.76	0.66	0.68			
	G	0.08	0.09	0.10			
3	N	0.32	0.30	0.27	3.90	2.49	1.56
	S	0.45	0.48	0.52			
	G	0.23	0.22	0.21			
4	N	0.65	0.48	0.44	3.43	2.20	1.56
	S	0.22	0.40	0.45			
	G	0.13	0.12	0.11			
5	N	0.39	0.31	0.29	4.86	3.40	1.43
	S	0.27	0.37	0.41			
	G	0.34	0.32	0.30			

<sup>a</sup> Terpolymer composition using quantitative  $^{13}\text{C}\{^1\text{H}\}$  = NMR spectroscopy.

<sup>b</sup> Terpolymer composition using statistical model using Alfrey–Goldfinger's equations.

<sup>c</sup>  $\bar{M}_w$  and  $\bar{M}_n$ , weight average and number average molecular weights.

<sup>d</sup> P, polydispersity.

quency of 300.13 and 75.5 MHz, respectively. The  $^1\text{H}$ -NMR spectrum was recorded by using the standard pulse sequence given in the Bruker pulse program library. The 32K data points were accumulated with 5 s as delay time between the 16 successive scans. A total of 6000 scans were accumulated with a relaxation delay of 2 s containing 16 K data points for the  $^{13}\text{C}$ .  $^{13}\text{C}\{^1\text{H}\}$ -NMR experiments were carried out by using the inverse-gated decoupling pulse program with 8 s as delay time. In both cases, the Waltz-16 broadband decoupler was used. The 2D proton-detected  $^1\text{H}$ - $^{13}\text{C}$ -HSQC spectrum was recorded by using the standard pulse sequence,<sup>17</sup> whereas the homonuclear TOCSY experiments were carried out with a Bruker 300 MHz spectrometer by using the standard pulse sequence.<sup>18</sup> A total of 32 scans were accumulated with relaxation delay of 2 s for each of the 512  $t_1$  experiments (where  $t_1$  is the increment in evolution time between pulses). Similarly, NOESY was recorded in predeuterated chloroform, with a Bruker 300 MHz DPX spectrometer using different standard pulse sequences; other related details are given in our earlier article.<sup>19–21</sup>

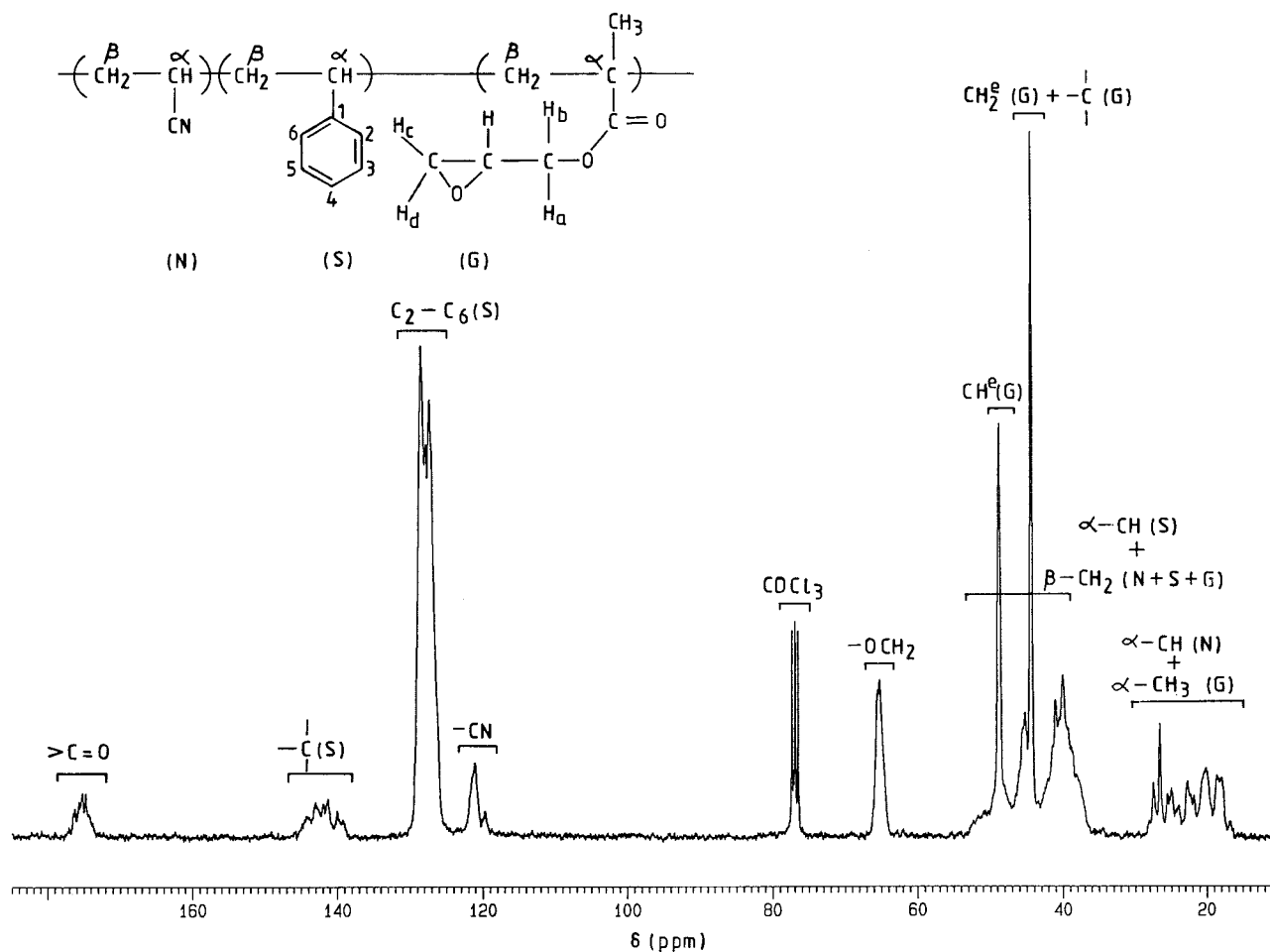
## RESULTS AND DISCUSSION

The monomer compositions of the acrylonitrile/styrene/glycidyl methacrylate (N/S/G) terpolymers were determined from the quantitative  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra and compared those with the compositions calculated from Goldfinger's equation<sup>22</sup> by using the reactivity ratios:  $r_{\text{NS}} = 0.04$ ,  $r_{\text{SN}} = 0.40$ ;  $r_{\text{NG}} = 0.22$ ,  $r_{\text{GN}} = 1.37$ ;  $r_{\text{SG}} = 0.44$ ,  $r_{\text{GS}} = 0.53$ . The average molecular

weights of the terpolymer with different compositions were determined by GPC in THF at  $30^\circ \pm 0.1^\circ$ . The terpolymer compositions and average molecular weights are shown in Table I.

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

Figure 1 shows the complete assignment of carbon resonance signals in  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the terpolymer N/S/G (N = 0.31, S = 0.37, and G = 0.32 mol % in the terpolymer) in  $\text{CDCl}_3$ . The spectral regions  $\delta 15.0$ – $30.0$  and  $\delta 35.0$ – $55.0$  ppm are complex and overlapping and can be assigned to aliphatic carbons in the main and branch chains of the terpolymer. The  $\alpha$ -methine carbon resonances of the N-monomeric unit are overlapping with the  $\alpha$ -methyl carbon of the G-unit. Further, the  $\alpha$ -methine carbon of S-unit and epoxy methine carbon of G-unit are overlapping with the epoxy methylene carbon of G-unit and  $\beta$ -methylene carbon resonances of N-, S-, and G-units. The signal at  $\delta 45.2$  ppm is assigned to quaternary carbon of G-unit, which is also overlapping with the methylene carbon resonances of the terpolymer. These overlapping carbon resonances can be assigned without ambiguity with the help of DEPT-135 (Fig. 2) and DEPT-90 (Fig. 3) experiments. In the DEPT-135 experiment, the methyl (G-monomeric unit), methine (S- and N-monomeric units), and epoxy methine (G-unit) carbon signals appear as positive phase, while the methylene (N-, S-, and G-units) and epoxy methylene (G-unit) appear as negative phase, respectively. In the DEPT-90 experiment, all the methine carbon signals appear as positive phase. The methylene carbon reso-

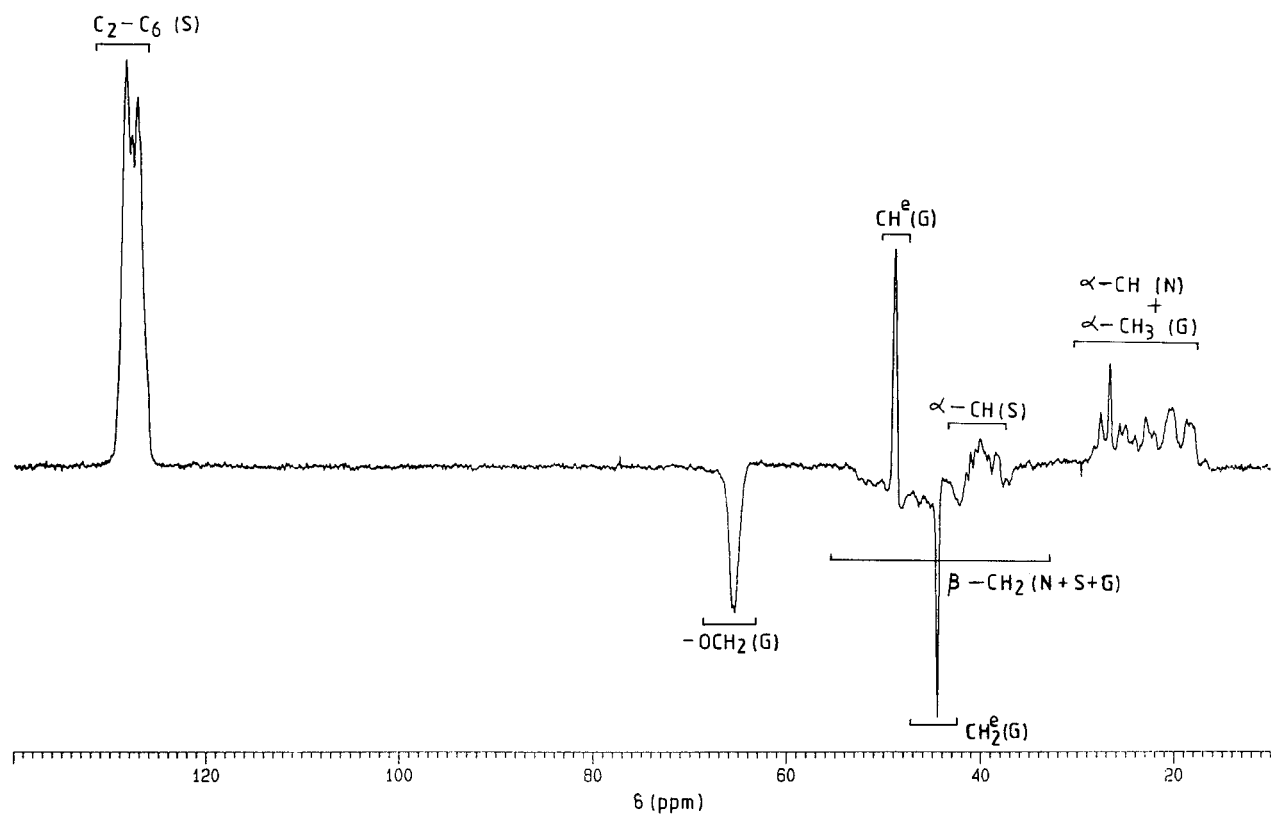


**Figure 1** The  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the acrylonitrile/styrene/glycidyl methacrylate terpolymer (N/S/G) (N = 0.31, S = 0.37, and G = 0.32 mol % in the terpolymer) in  $\text{CDCl}_3$ .

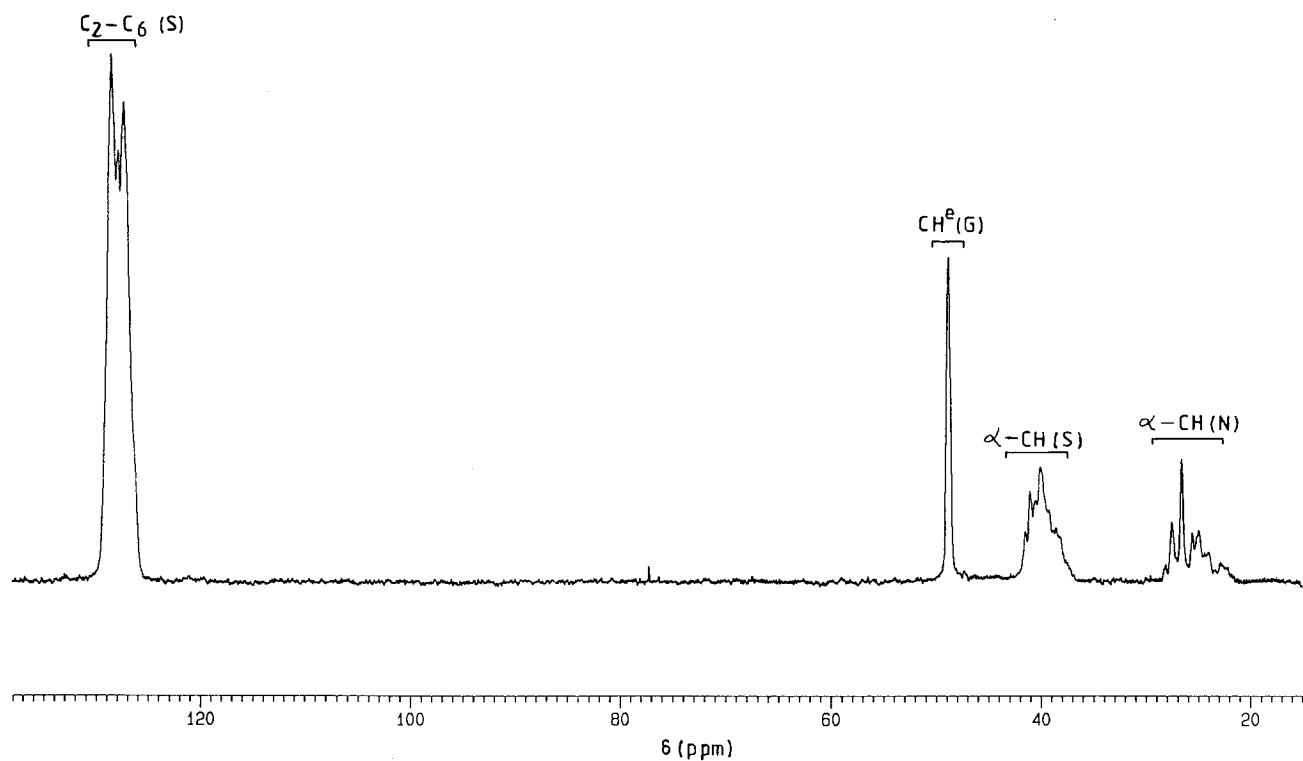
nances of N-, S-, and G-units can be assigned around 833.0–56.0 ppm. The signals around  $\delta$ 21.5–29.0 and  $\delta$ 37.0–43.0 ppm can be assigned to methine carbon resonances of N- and S-monomeric units, respectively. The methyl carbon of the G-unit in the terpolymer resonates around  $\delta$ 16.0–23.5 ppm. The signals at  $\delta$ 48.7 and  $\delta$ 44.4 ppm are due to epoxy methine and epoxy methylene carbon resonances of G-monomeric unit in the terpolymer. The oxymethylene carbon resonates around  $\delta$ 63.5–67.0 ppm. The methyl carbon signals of the G-unit show compositional sensitivity. The methine carbon resonances of N- and S-units also show compositional triad sensitivity.

The nitrile carbon resonance signals around  $\delta$ 118.0–123.5 ppm are sensitive to the distribution of the N-centered triad sequences. The expanded signal around  $\delta$ 138.0–146.0 ppm is assigned to quaternary carbon in the phenyl group of the S-unit. The signals around  $\delta$ 173.0–178.5 ppm are due to carbonyl carbon resonances. All the resonance signals were assigned by comparing with the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the N/S, S/G, and N/G copolymers.

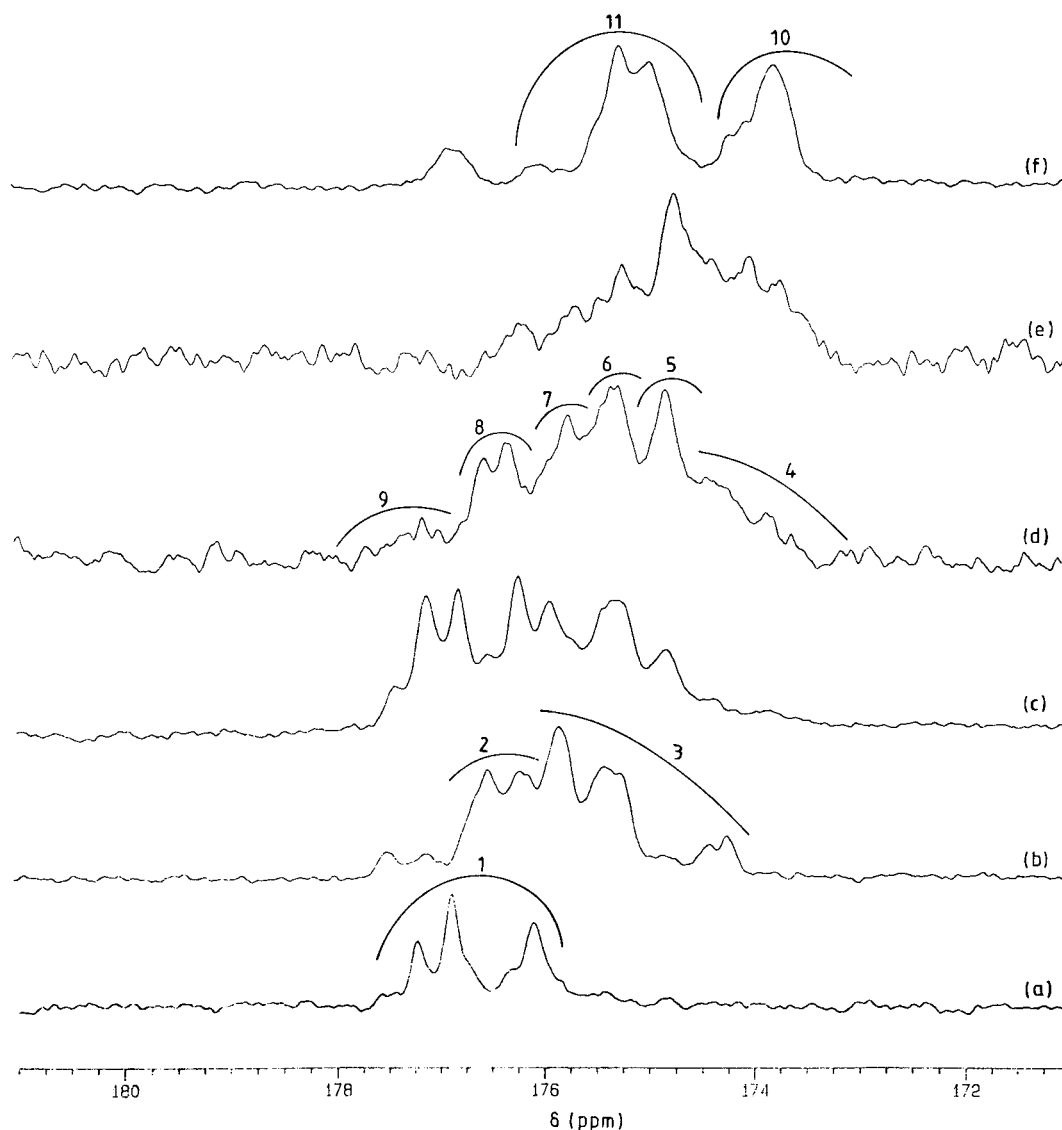
The expanded  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the carbonyl carbon resonances of the N/S/G terpolymers are shown in Figure 4. The spectra of terpolymers show signals of homopolymer and copolymers along with some new signals. All the signals could be assigned to G-centered compositional sequences. The assignments to various signals are done with the help of the spectra of individual homopolymer (PGMA) and copolymers (S/G and N/G) and by observing change in intensity of signals with the change in composition of terpolymers. In the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of poly(glycidyl methacrylate), the signals around  $\delta$ 175.6–177.9 ppm (1) is assigned to GGG triad. There are two broad envelopes in the carbonyl carbon region around  $\delta$ 174.0–175.9 (3) and  $\delta$ 175.9–176.8 (2) ppm are assigned to SGS and GGS triads in the styrene/glycidyl methacrylate (S/G) copolymer. Similarly, the signals around  $\delta$ 173.25–174.40 (10) and  $\delta$ 174.40–176.15 (11) ppm are assigned to NGN and NGG triads in the acrylonitrile/glycidyl methacrylate (N/G) copolymer, by comparing the carbonyl carbon resonance signals of poly(glycidyl methacrylate). The signals around



**Figure 2** The DEPT-135 spectrum of the acrylonitrile/styrene/glycidyl methacrylate terpolymer (N/S/G) (N = 0.31, S = 0.37, and G = 0.32 mol % in the terpolymer) in  $\text{CDCl}_3$ .



**Figure 3** The DEPT-90 spectrum of the acrylonitrile/styrene/glycidyl methacrylate terpolymer (N/S/G) (N = 0.31, S = 0.37, and G = 0.32 mol % in the terpolymer) in  $\text{CDCl}_3$ .

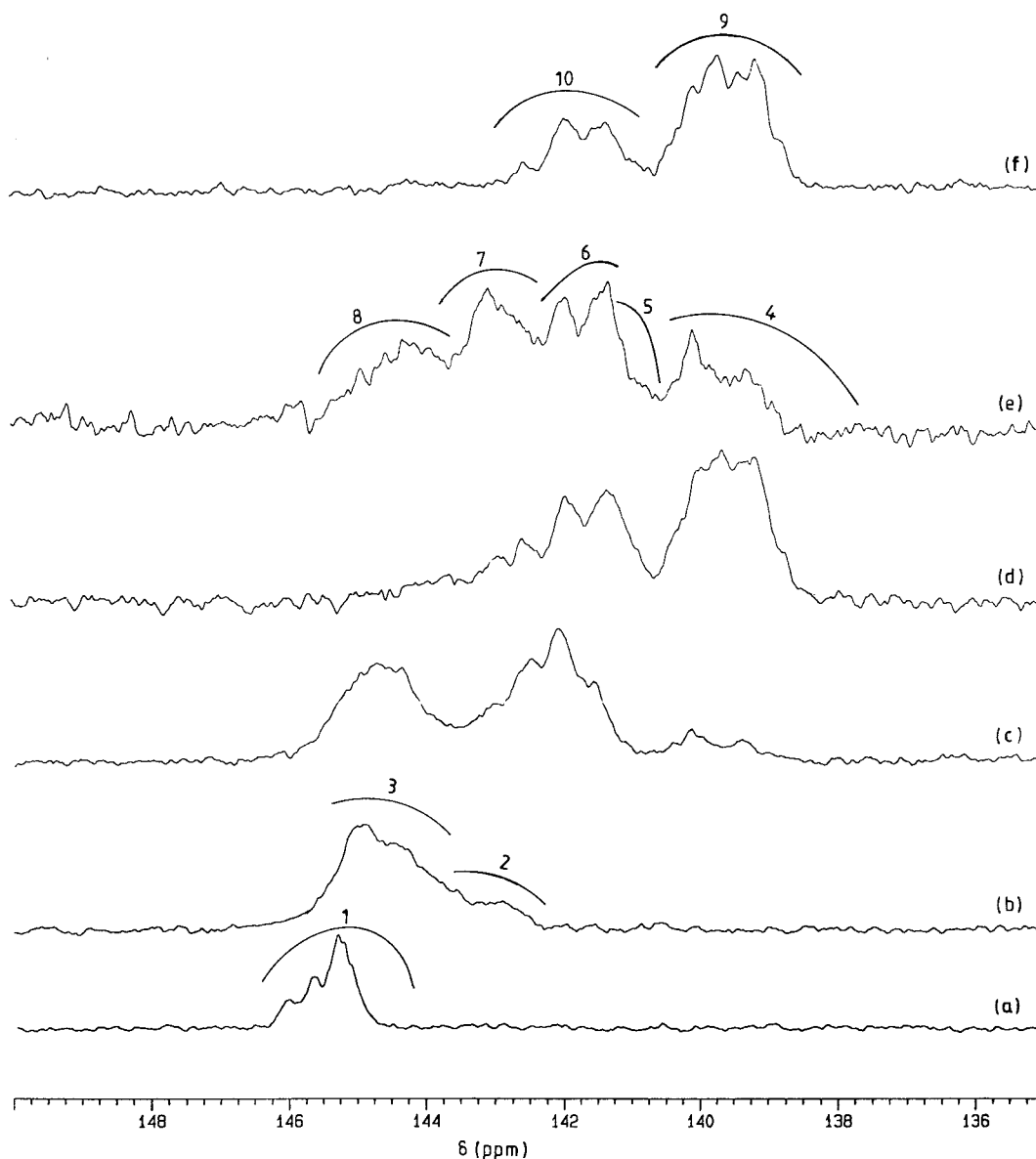


**Figure 4** The expanded  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the carbonyl carbon region of (a) PGMA; (b) S/G copolymer (0.47 : 0.53); terpolymer (N =, S =, and G = mol %s in the terpolymer); (c) 0.14 : 0.19 : 0.67; (d) 0.31 : 0.37 : 0.32; (e) 0.48 : 0.40 : 0.12; and (f) N/G copolymer (0.52 : 0.48) in  $\text{CDCl}_3$ .

$\delta 173.15\text{--}174.45$  (4) and  $\delta 174.45\text{--}175.20$  (5) ppm, which show the increase in intensity of the signals with increase in the concentration of the N-unit and decrease in the concentration of G-unit and are assigned to NGN and NGG triads in the N/S/G terpolymer. The resonance signal at  $\delta 175.20\text{--}175.70$  (6) ppm is due to NGS triad. Similarly, the resonance signals around  $\delta 175.70\text{--}176.10$  (7) and  $\delta 176.10\text{--}176.80$  (8) ppm, which show an increase in the intensity of the signals with the increase in the concentration of S-unit and decrease in the concentration of G-unit, are assigned to SGS and GGS triads in the terpolymer. The region  $\delta 176.80\text{--}177.9$  (9) ppm is assigned to the GGG triad of the terpolymer.

The expanded  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the quaternary carbon resonances of S-unit in the N/S/G terpolymers are shown in Figure 5. The quaternary re-

gion of the S-unit of  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum is showing multiplets and can be assigned to compositional sequences. There are some new signals of terpolymers along with the signals of polystyrene and copolymers (S/G and N/S). All the signals could be assigned to S-centered compositional sequences. The assignments to various signals are done with the help of the spectra of individual homopolymer (PS) and copolymers (N/S and S/G), and by observing the change in intensity of the signals with the change in composition of terpolymers. In the  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of polystyrene, the signals around  $\delta 144.5\text{--}146.5$  (1) ppm are assigned to SSS triad. There are two broad envelopes in the quaternary carbon region around  $\delta 142.75\text{--}144.20$  (2) and  $\delta 144.20\text{--}145.90$  (3) ppm are assigned to GSG and SSG triads in the styrene/glycidyl methacrylate copoly-



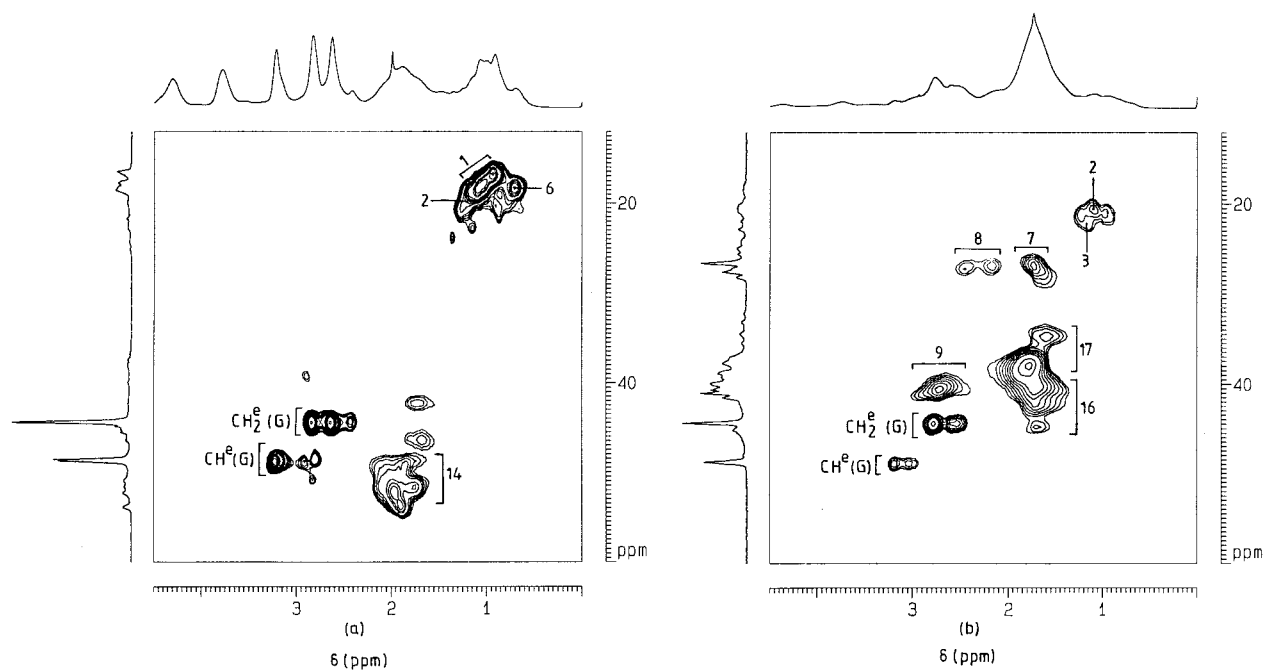
**Figure 5** The expanded  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the quaternary carbon region of (a) PS; (b) S/G copolymer (0.48 : 0.52); terpolymer (N =, S =, and G = mol %s in the terpolymer); (c) 0.25 : 0.66 : 0.09; (d) 0.48 : 0.40 : 0.12; (e) 0.31 : 0.37 : 0.32; and (f) N/S copolymer (0.56 : 0.40) in  $\text{CDCl}_3$ .

mer. Similarly, the signals around  $\delta 138.50$ – $140.75$  (9) and  $\delta 140.75$ – $143.25$  (10) ppm are assigned to NSN and NSS triads in the acrylonitrile/styrene (N/S) copolymer, by comparing the quaternary carbon resonance signals of polystyrene. The signals around  $\delta 138.30$ – $141.25$  (4) and  $\delta 141.25$ – $141.75$  (5) ppm, which show the increase in intensity of the signals with increase in the concentration of the N-unit and decrease in the concentration of S-unit, are assigned to NSN and NSS triads in the N/S/G terpolymer. The resonance signal at  $\delta 141.75$ – $142.75$  (6) ppm is assigned to NSG triad. Similarly, the resonance signals around  $\delta 142.75$ – $144.25$  (7) ppm, which show increase in the intensity of the signals with the increase in the concentration of G-unit and decrease in the concentration of S-unit, is assigned to GSG triad in the terpoly-

mer. In the region  $\delta 144.25$ – $146.40$  (8) ppm, there is decrease in intensity of the signals with the increase in the concentration of G-unit and decrease in the concentration of S-unit and is assigned to SSG triad in the N/S/G terpolymer.

## 2D HSQC NMR studies

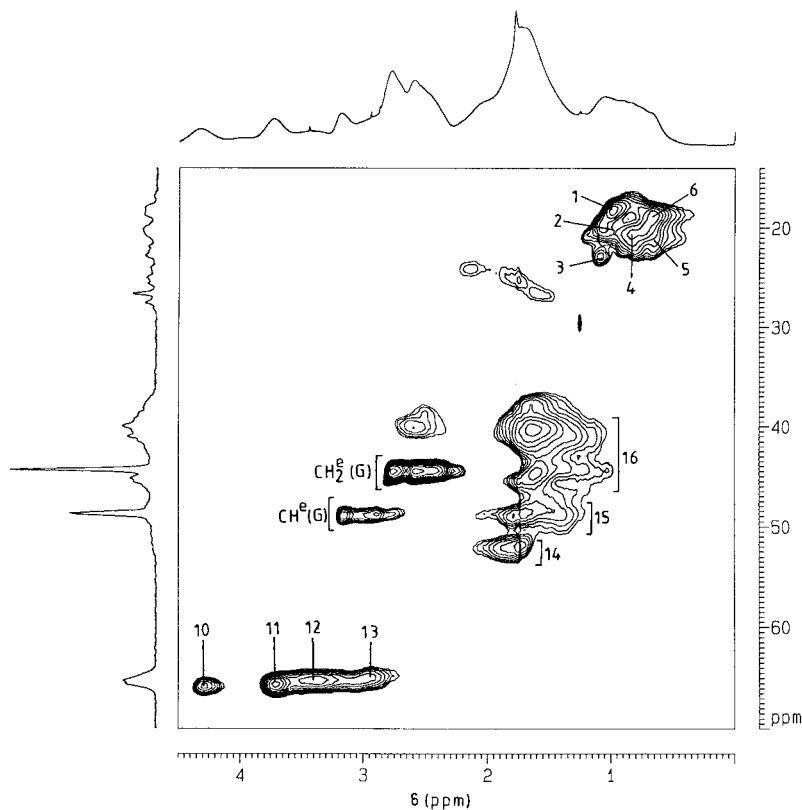
The  $\alpha$ - $\text{CH}_3$  region in 1D ( $^1\text{H}$ ) and  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the terpolymers is quite complex and overlapped. This region can be assigned with the help of 2D HSQC NMR spectra. Figures 6(a, b) and 7 show the 2D  $^{13}\text{C}$ - $^1\text{H}$ -HSQC NMR spectra of three different compositions of the N/S/G terpolymer. It is observed that in the S/G copolymers, the S-unit adjacent to the



**Figure 6** The 2D HSQC spectra of the N/S/G terpolymers with compositions (N =, S =, G = mol %s in the terpolymer); (a) 0.14, 0.19, 0.67; and (b) 0.48, 0.40, 0.12.

G-centered triad leads to the shielding of both oxymethylene and carbonyl carbons (SGS < GGS < GGG, in increasing order of chemical shifts), but methyl

carbon follows the reverse arrangement in the triads distribution (GGG < GGS < SGS). In the N/G copolymers, addition of the acrylonitrile unit adjacent to the



**Figure 7** The 2D HSQC spectrum of the N/S/G terpolymer (N = 0.31, S = 0.37, G = 0.32 mol % in the terpolymer) in CDCl<sub>3</sub>.

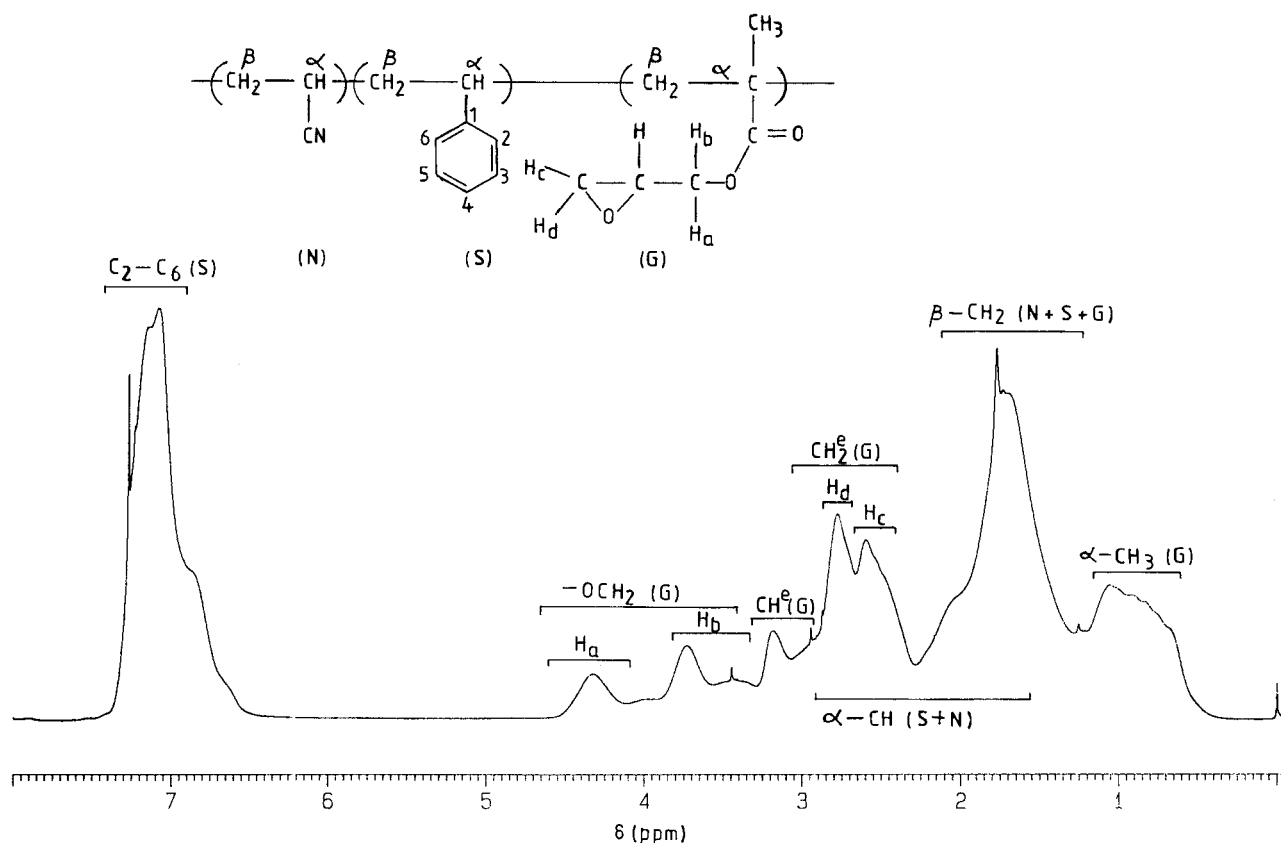
**TABLE II**  
**The Compositional Assignments of  $\alpha$ -CH<sub>3</sub>,  $\alpha$ -CH, -OCH<sub>2</sub>, and  $\beta$ -CH<sub>2</sub> Carbon Resonance Signals from 2D HSQC NMR Spectra of N/S/G Terpolymers**

Sample No.	Chemical shift( $\delta$ ), ppm	Assignment
		$\alpha$ -CH <sub>3</sub>
1	15.5–19.0/0.85–1.05	GGG
2	19.0–21.5/1.05–1.20	NGG
3	21.5–23.8/1.12	NGN
4	20.8/0.80–0.95	NGS
5	21.4/0.64–0.45	SGS
6	17.5–19.5/0.65–0.80	GGG
		$\alpha$ -CH
7	25.5–28.5/1.60–1.88	SNS
8	26.0–28.0/2.05–2.55	NNS
9	39.0–42.0/2.45–2.95	NSN
		-OCH <sub>2</sub>
10	65.6/4.38	GGG (a)
11	65.4/3.70	GGG (b)
12	65.0/3.20–3.55	GGG
13	64.9/2.75–3.20	SGS
		$\beta$ -CH <sub>2</sub>
14	50.5–53.5/1.60–2.08	GG
15	47.5–50.5/1.20–1.95	SG
16	39.5–47.5/1.10–2.05	NG + SS
17	33.2–39.5/1.35–2.15	NN + NS

G-centered triad leads to the shielding of the carbonyl carbon (NGN < NGG < GGG, in the increasing order of chemical shifts), at the same time deshielding of the

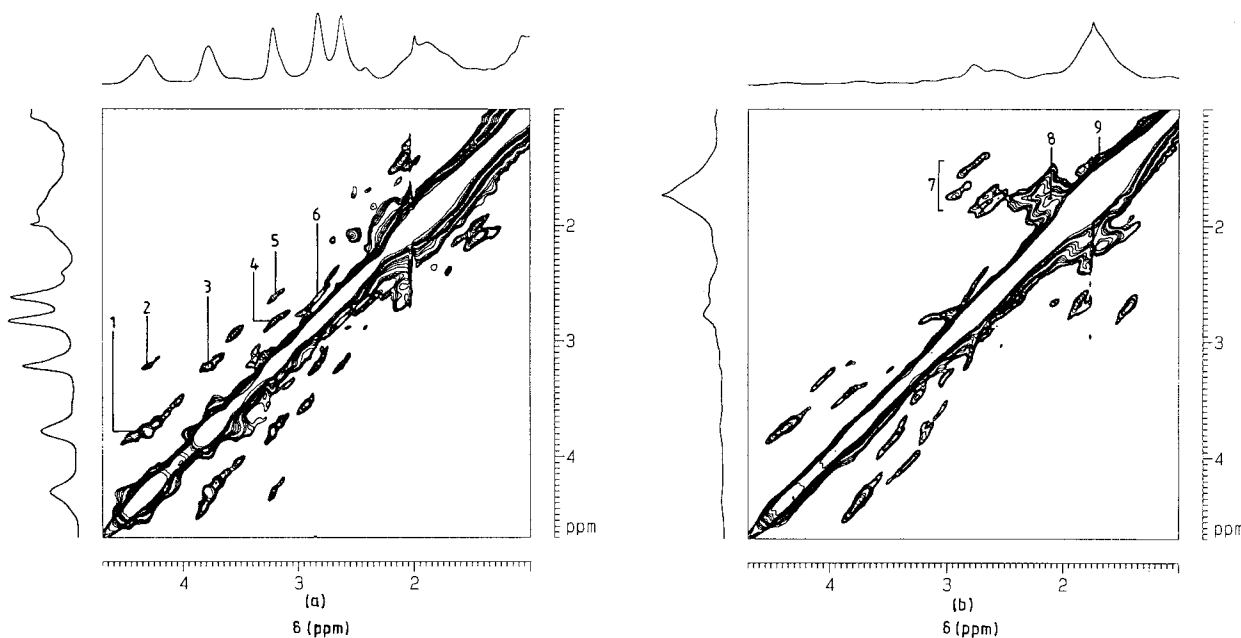
methyl carbons of G-centered triads. So, it follows the reverse trend for the methyl carbons of G-centered triads (GGG < NGG < NGN). The  $\alpha$ -CH<sub>3</sub> group in the G-monomeric unit of the terpolymer shows compositional sensitivity. The assignments of the methyl carbon resonance of the terpolymer are done on the basis of the change in intensity of the signals with change in the composition of the terpolymers and by comparing the methyl carbon resonances in the HSQC spectra of the styrene-glycidyl methacrylate (S/G) and acrylonitrile-glycidyl methacrylate (N/G) copolymers. The cross peak at  $\delta$  15.5–19.0/0.85–1.05 (1) is assigned to GGG triad, on the basis of the assignment done in the HSQC spectrum of poly(glycidyl methacrylate), while the other cross peaks at  $\delta$  19.0–21.5/1.05–1.20 (2) and  $\delta$  21.5–23.8/1.12 (3) ppm are assigned to NGG and NGN triads. The cross peak at  $\delta$  20.8/0.80–0.95 (4) ppm is due to NGS triad. Similarly, the cross peaks at  $\delta$  21.4/0.64–0.45 (5) and  $\delta$  17.5–19.5/0.65–0.80 (6) are assigned to SGS and GGS triads.

The methine carbon signals in the N-monomeric unit of the terpolymer show compositional sequences. The cross peaks at  $\delta$  25.5–28.5/1.60–1.88 (7) and  $\delta$  26.0–28.0/2.05–2.55 (8) ppm are assigned to SNS and NNS triads, respectively, on the basis of change in intensity of the signals with change in terpolymer composition and by comparing the HSQC spectrum of



**Figure 8** The proton NMR spectrum of the N/S/G terpolymer (N = 0.31, S = 0.37, and G = 0.32 mol % in the terpolymer).





**Figure 9** The 2D TOCSY spectra of the N/S/G terpolymers with compositions (N = , S = , G = mol %s in the terpolymer); (a) 0.14, 0.19, 0.67; and (b) 0.48, 0.40, 0.12 at low mixing time (4 ms).

N/S copolymer. The SNS triad has lower chemical shift because the increased bulkiness of the S-unit on either side of the N-centered unit leads to the shielding of the methine proton of the acrylonitrile unit (NNN > NNS > SNS).

The cross peak at  $\delta 39.0\text{--}42.0/2.45\text{--}2.95$  (9) ppm is assigned NSN triad, on the basis of change in intensity of the signals with the terpolymer compositions and by comparing the HSQC spectrum of N/S copolymer.

The oxymethylene carbon resonances of the G-unit in the terpolymer can be assigned to compositional triad sequences. The cross peaks at  $\delta 65.5/4.38$  (10) and  $\delta 65.4/3.70$  (11) ppm are assigned to GGG (a) and GGG (b) triads, on the basis of change in intensity of signals with change in terpolymer compositions and by comparing the HSQC spectrum of poly(glycidyl methacrylate). The addition of the styrene unit to the G-centered triad increases the shielding of the oxymethylene region in the N/S/G terpolymer and this can be assigned at  $\delta 65.0/3.20\text{--}3.55$  (12) and  $\delta 64.9/2.75\text{--}3.20$  (13) ppm to GGS and SGS triads.

The epoxy methylene proton region is assigned around  $\delta 44.5/2.30\text{--}2.95$  ppm and shows compositional sensitivity. The peak positions of triad sequence in various compositional sequences are overlapped and cannot be resolved, and hence, are difficult to assign.

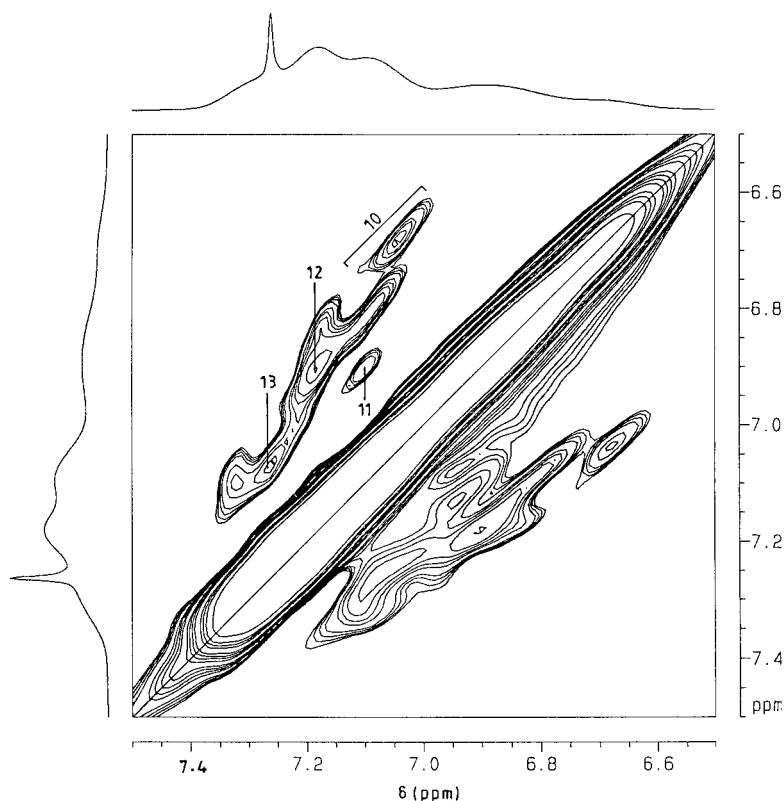
The methylene carbons in six different chemical environments can be divided into broad NN, NS, NG, SS, SG, and GG dyads on the basis of change in intensity of signals with change in terpolymer composition and by comparing the three different N/S, N/G, and S/G copolymers. These dyads are assigned as GG

> SG > SS > NG > NS > NN, in the decreasing order of chemical shifts. Because of overlapping of the methylene carbon signals, there are few assignments observed in the methylene carbon region. The cross peaks region around  $\delta 50.5\text{--}53.5/1.60\text{--}2.08$  (14),  $\delta 47.5\text{--}50.5/1.20\text{--}1.95$  (15),  $\delta 39.5\text{--}47.5/1.10\text{--}2.05$  (16), and  $\delta 33.2\text{--}39.5/1.35\text{--}2.15$  (17) ppm are assigned to GG, SG, NG + SS, and NN + NS dyads, respectively. All the assignments are shown [Figs. 6(a, b) and 7] in Table II.

#### <sup>1</sup>H and 2D-TOCSY spectra studies

The proton spectrum of the terpolymer N/S/G along with signal assignments is shown in Figure 8 (N = 0.31, S = 0.37, and G = 0.32 mol % in the terpolymer). After assigning the <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum completely, the various overlapping resonance signals in <sup>1</sup>H-NMR spectrum are assigned by a one-to-one correlation between carbon and proton with the help of 2D HSQC NMR spectrum. To understand the connectivity and to confirm the various couplings in the terpolymer chain, the TOCSY spectra (at low mixing time, 4 ms) were recorded in CDCl<sub>3</sub>, as shown in Figure 9(a, b).

The two protons of —OCH<sub>2</sub> in the G-unit of the terpolymer are diastereomeric and are coupled to each other. The cross peak at  $\delta 3.80/4.32$  (1) ppm is due to coupling of proton b with proton a of —OCH<sub>2</sub> unit in GGG triad. The cross peaks at  $\delta 3.24/4.30$  (2) and  $\delta 3.23/3.78$  (3) are due to coupling of epoxy methine proton with protons a and b of the OCH<sub>2</sub> group. Similarly, the d and c protons of epoxy methylene group are coupling with the epoxy methine proton at



**Figure 10** The aromatic region of 2D TOCSY spectrum of the N/S/G terpolymer (N = 0.48, S = 0.40, and G = 0.12 mol % in the terpolymer).

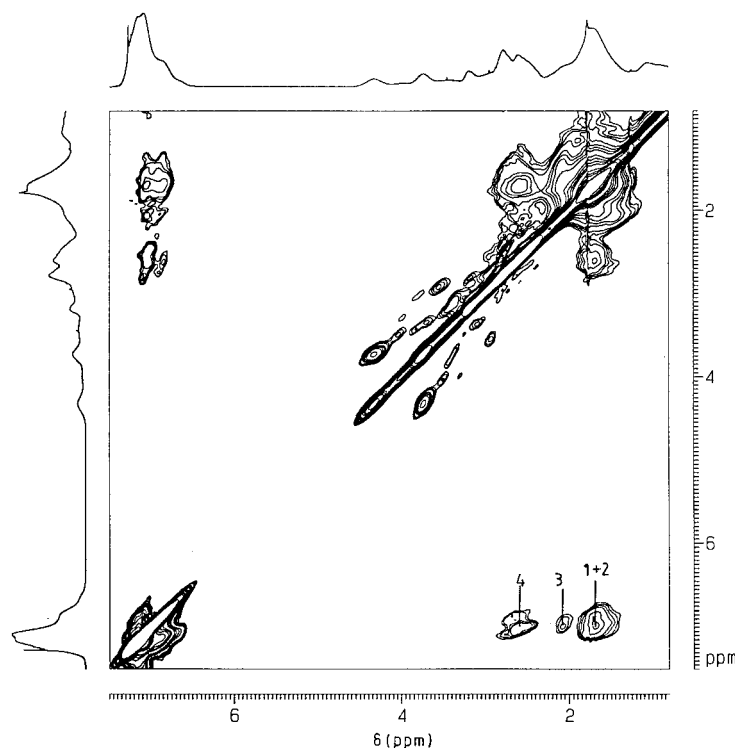
$\delta$ 2.85/3.24 (4) and  $\delta$ 2.64/3.21 (5) ppm. The proton c couples with proton d at  $\delta$ 2.65/2.85 (6) ppm. Three-bond coupling between the methine proton of the NSN triad and the methylene protons of NS dyad gives the cross peak at  $\delta$ 2.48–2.98/1.35–1.92 (7) ppm. In the NNS triad region, the central methine proton of NNS triad shows three-bond coupling with the methylene protons of NN dyad at  $\delta$ 2.08/1.80 (8) ppm. Similarly, the coupling between the methine proton of

SNS triad and methylene protons of NS dyad gives the cross peak region around  $\delta$ 1.73/1.45 (9) ppm.

The coupling within the aromatic protons of the styrene unit is also possible and appears as multiplets (Fig. 10). The multiplets can be assigned to coupling of aromatic protons in different compositional sequences. The signals around  $\delta$ 6.88–7.10/6.60–6.81 (10),  $\delta$ 7.10/6.90 (11),  $\delta$ 7.10–7.30/6.81–6.96 (12), and  $\delta$ 7.23–7.35/7.02–7.14 (13) ppm are assigned

**TABLE III**  
TOCSY  $^1\text{H}$ – $^1\text{H}$  Shift Correlation with Assignments in N/S/G Terpolymer

Peak No.	Type of proton (ppm)	Coupled to proton (ppm)	
1	b proton in GGG triad (3.80)	a proton in GGG triad (4.32)	
2	Epoxy methine proton (3.24)	a proton in GGG triad (4.30)	
3	Epoxy methine proton (3.23)	b proton in GGG triad (3.78)	
4	d proton in epoxy methylene group (2.85)	Epoxy methine proton (3.24)	
5	c proton in epoxy methylene group (2.64)	Epoxy methine proton (3.21)	
6	c proton in epoxy methylene group (2.65)	d proton in epoxy methylene group (2.85)	
7	CH proton in NSN triad (2.48–2.98)	CH <sub>2</sub> proton in NS dyad (1.35–1.98)	
8	CH proton in NNS triad (2.08)	CH <sub>2</sub> proton in NN dyad (1.80)	
9	CH proton in SNS triad (1.73)	CH <sub>2</sub> proton in NS dyad (1.45)	
	Aromatic region		Assignments
10	6.88–7.10	6.60–6.81	SSS + SSG
11	7.10	6.90	GSG
12	7.10–7.30	6.81–6.96	NSS
13	7.23–7.35	7.02–7.14	NSN



**Figure 11** The 2D NOESY spectrum of the N/S/G (N = 0.31, S = 0.37, and G = 0.32 mol % in the terpolymer) terpolymer.

to SSS + GSS, GSG, NSS, and NSN triads, by comparing the TOCSY spectra of N/S, S/A copolymers. All the assignments [Figs. 9(a, b) and 10] are shown in Table III.

### 2D NOESY spectrum studies

Figure 11 shows the 2D NOESY spectrum of the N/S/G (N = 0.31, S = 0.37, and G = 0.32 mol % in the terpolymer) terpolymer. The mixing time of 350 ms was found to be optimum, as there was no spin diffusion. The spatial coupling between the methylene protons of the NS dyad with phenylic protons of the styrene unit show the cross peak region around  $\delta$ 1.45–1.90/6.65–7.10 (1) ppm. The methylene protons in the SNS, NNS, and NSN triads coupled spatially with the ortho protons of the styrene units, giving rise to cross peaks at  $\delta$ 1.72/6.98 (2),  $\delta$ 2.09/6.94 (3), and  $\delta$ 2.40–2.80/7.05 (4) ppm, respectively.

### CONCLUSION

The compositions of the N/S/G terpolymers obtained from quantitative  $^{13}\text{C}\{^1\text{H}\}$ -NMR are in good agreement with those calculated by Goldfinger's equation. The sequence distribution of the acrylonitrile/styrene/glycidyl methacrylate terpolymers is analyzed by 1D and 2D NMR techniques. The methyl, methine, and oxymethylene carbon resonances are assigned to triad, whereas the methylene carbon resonances are

assigned to dyad compositional sequences with the help of 2D-HSQC spectra. The heteronuclear  $^{13}\text{C}$ - $^1\text{H}$  HSQC NMR spectra gave unambiguous assignment of the  $^1\text{H}$ -NMR spectrum of the terpolymer, and the homonuclear 2D ( $^1\text{H}$ - $^1\text{H}$ ) TOCSY NMR spectra suggested the various structural arrangements of the polymer chains. 2D NOESY spectrum is used to assign the spatial interaction between the phenylic protons and the methylene protons of respective triads and dyads.

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