

# Two-Dimensional NMR Studies of Styrene/*n*-Butyl Acrylate Copolymers Synthesized by Atom Transfer Radical Polymerization

A. S. Brar, Puneeta

Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110 016, India

Received 16 February 2005; accepted 29 June 2005

DOI 10.1002/app.22816

Published online 19 December 2005 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Copolymers of styrene and *n*-butyl acrylate were prepared by atom transfer radical polymerization (ATRP) using CuBr/*N,N,N',N',N''*-pentamethyl-diethylenetriamine as catalyst and Methyl 2-bromopropionate as initiator. The polydispersity of the copolymers is quite low (1.1–1.3).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectra of these copolymers show that the methylene and methine signals of the main chain are compositional sensitive and highly overlapped. Even the distortionless enhancement by polarization transfer (DEPT)

was not able to assign the complex and overlapping signals. Assignments of the various resonance signals were done with the help of heteronuclear single quantum coherence (HSQC), total correlation spectroscopy (TOCSY), and heteronuclear multiple bond correlation (HMBC) experiments. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2694–2701, 2006

**Key words:** styrene/*n*-butyl acrylate copolymer; 2D-NMR; microstructure; sequence distribution

## INTRODUCTION

Copolymers of styrene and *n*-butyl acrylate (S/B) have attracted great deal of interest in the recent past because of their wide applications, mostly, in adhesives and coating industries. Free-radical polymerization is one of the most versatile method of preparing copolymers, but, it has been limited by the inevitable, fast, and irreversible termination of the growing radicals by the coupling and disproportionation reactions, leading to the poor control of the reaction and high polydispersity of the resulting polymer. Thus, much research has been devoted to develop a controlled radical polymerization method to synthesize well-defined polymers with narrow molecular weight distributions and desired complex architectures.<sup>1</sup> One of the most successful method has been atom transfer radical polymerization (ATRP).<sup>2–4</sup> This technique is versatile and has successfully been applied to vinyl monomers such as acrylates,<sup>5,6</sup> methacrylates,<sup>7–9</sup> and styrene(s)<sup>10</sup> to prepare polymers with controlled molecular weights and well-defined structures.<sup>11</sup> A successful ATRP will not only have a small contribution of terminated chains, but also a uniform growth of all the chains, which is through fast initiation and rapid

reversible deactivation. Therefore, the molecular weight distributions are narrow with the polydispersity index ( $M_w/M_n$ ) similar to that of living polymerization. Copolymers of styrene and *n*-butyl acrylate were prepared by ATRP having low polydispersity ( $M_w/M_n = 1.1–1.3$ ).

Knowledge of the microstructure of the polymers is very important for understanding the relation between structure and property. High-resolution one-dimensional (1D) NMR<sup>12,13</sup> spectroscopy has proven to be a very informative technique for the structure elucidation, but in case of polymers, generally, overlapping signals are observed due to various compositional and configurational sequences. Thus, two-dimensional (2D) NMR techniques are required to resolve the signals. Various 2D NMR<sup>14–16</sup> experiments, especially HSQC and TOCSY experiments, have been used to assign the microstructure of the polymers<sup>17–24</sup> in terms of compositional and configurational sequences.

In this manuscript, we report the microstructure of styrene/*n*-butyl acrylate(S/B) copolymer, with the help of various two-dimensional NMR techniques. Earlier, Guzman et al.<sup>25</sup> reported the structure of S/B copolymers by  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR prepared by emulsion polymerization. In continuation of the earlier investigation, we have already reported the one dimensional NMR studies of the S/B copolymer in our earlier publication.<sup>26</sup> The  $^1\text{H}$  and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectra of the S/B copolymers are very complex, and it was difficult to ascertain various compositional and configurational sequences only by one dimensional NMR spectroscopy.

Correspondence to: A. S. Brar (asbrar@chemistry.iitd.emet.in).

Contract grant sponsor: Council of Scientific and Industrial Research (CSIR).

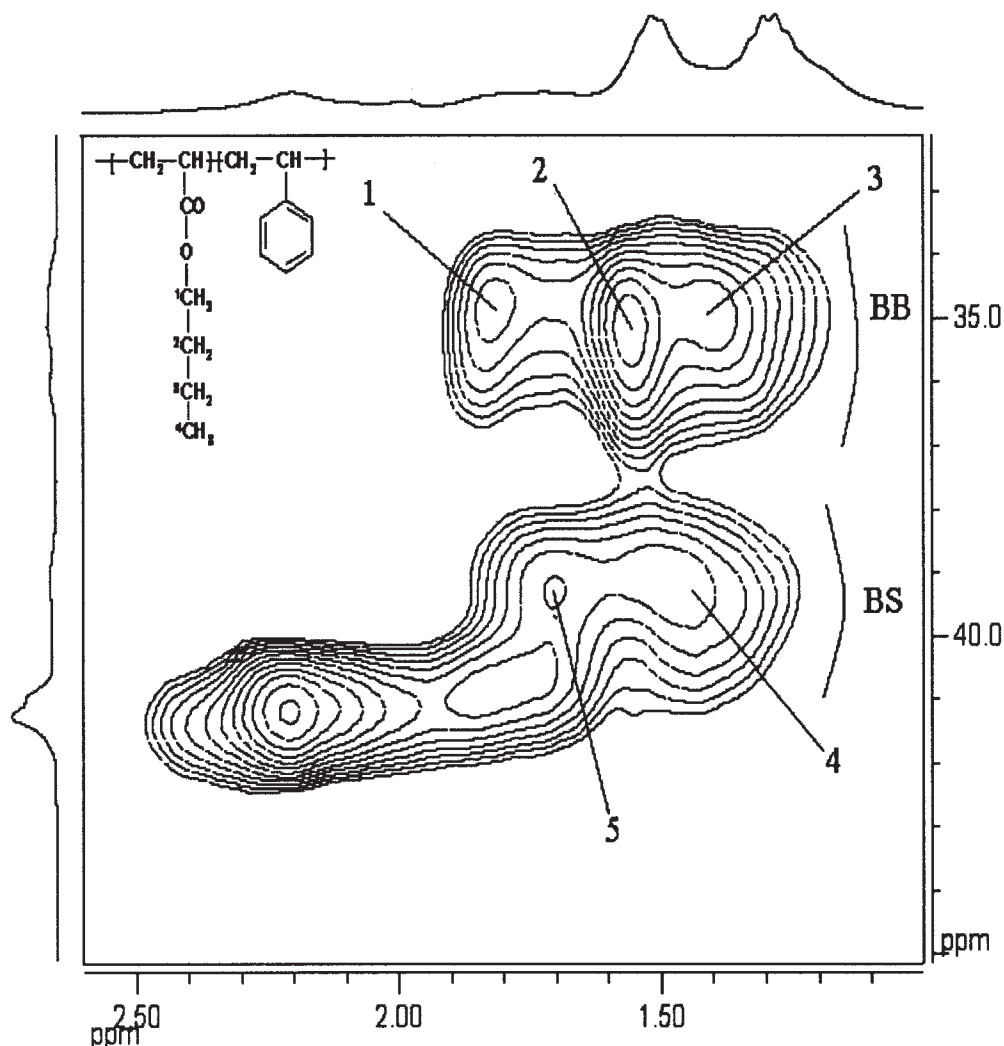


Figure 1 Expanded HSQC spectrum of S/B copolymer ( $F_B = 0.80$ ) in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

copy. The complete assignment of the complex and overlapping  $^1\text{H}$  and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectra of S/B copolymers in terms of compositional sequences are done with the help of two-dimensional HSQC, TOCSY, and HMBC experiments.

### EXPERIMENTAL

*n*-Butyl acrylate (CDH) and styrene were distilled under reduced pressure to remove inhibitors and stored below  $5^\circ\text{C}$ . Methyl 2-bromopropionate (Aldrich, 98%) was distilled at reduced pressure.  $N,N,N',N',N''$ -Pentamethyldiethylenetriamine, PMDETA (Aldrich, 99%), copper(I) bromide (CuBr; Aldrich, 98%), and copper metal powder (Cu(0), CDH, 99.5%) were used as such. Chloroform was dried over Phosphorus pentoxide and distilled. Methanol was dried over Calcium chloride and distilled.

Copolymers of styrene and *n*-butyl acrylate were prepared by ATRP as reported in our previous publi-

cation.<sup>26</sup> The resulting copolymers were dried under vacuum at  $78^\circ\text{C}$  for 24 h.

### NMR measurements

All the NMR spectra were recorded in  $\text{CDCl}_3$  at  $25^\circ\text{C}$  on a Bruker DPX-300 NMR spectrometer operating at 300.13 and 75.48 MHz for  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, respectively, using the standard pulse sequences. Gradient heteronuclear single quantum coherence (HSQC) experiment was performed using the standard Bruker *invigptp* pulse sequence. The spectrum was obtained with 512 increments in the  $F_1$  dimension and 2048 data points in the  $F_2$  dimension. Total correlation spectroscopy (TOCSY) experiment was carried out using standard pulse sequence. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512  $t_1$  experiments (where  $t_1$  is the increment in evolution time between pulses). Gradient heteronuclear multiple bond correlation (HMBC) experiment was

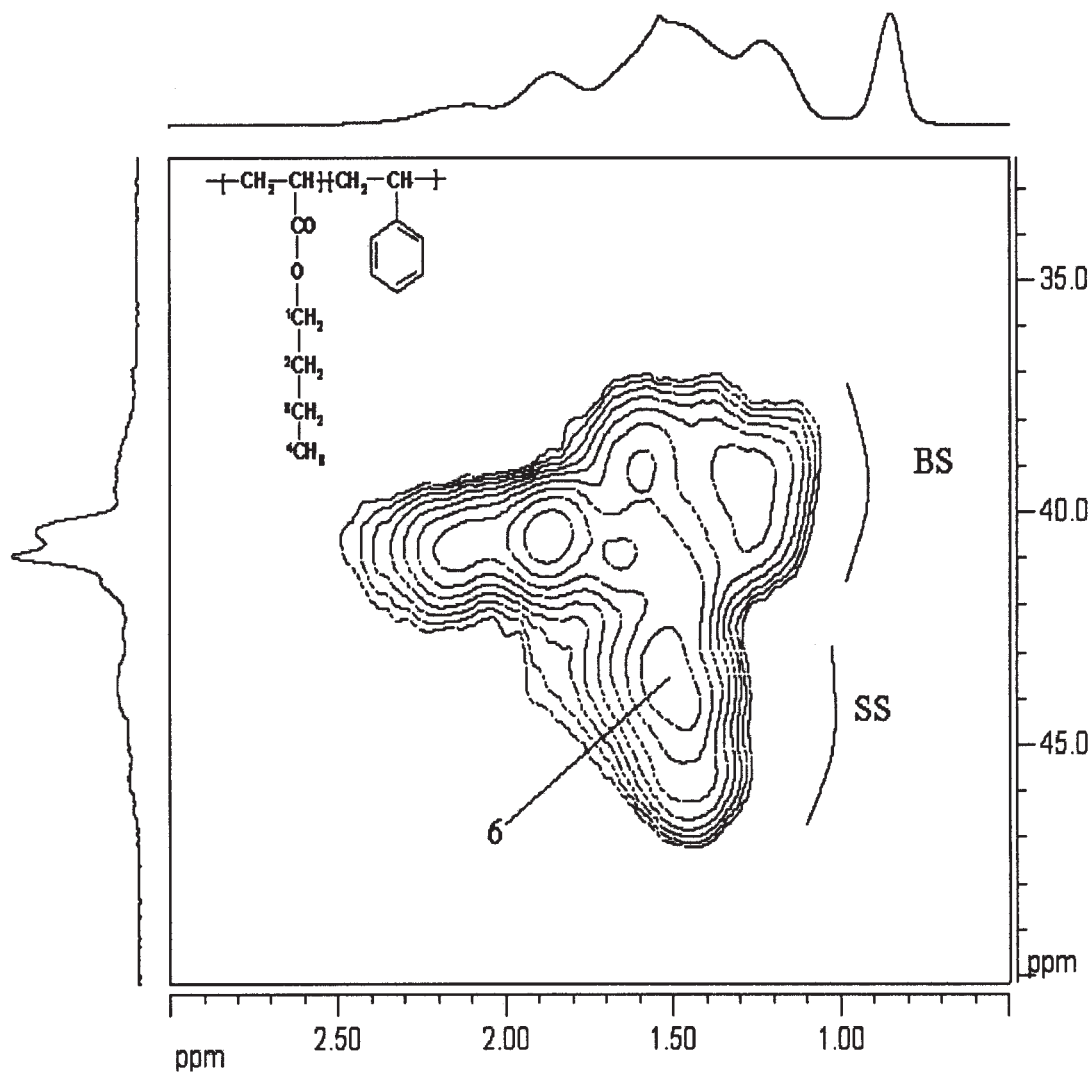


Figure 2 Expanded HSQC spectrum of S/B copolymer ( $F_B = 0.22$ ) in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

performed using the standard Bruker *inv4gplplrnd* pulse sequence.

## RESULTS AND DISCUSSION

### 2D HSQC studies

HSQC NMR spectrum of S/B copolymer is very complex. Resonance signals of the main chain methine and methylene groups of both styrene and *n*-butyl acrylate units are overlapping. Therefore, it is very difficult to determine the microstructure of S/B copolymer as such. However, on the basis of variation in the composition of the copolymers, and on comparison with the spectra of poly(*n*-butyl acrylate) and poly(styrene), the various compositional and configurational sequences are assigned. Expanded 2D HSQC NMR spectra showing methylene and methine carbon signals of the two different compositions of the S/B copolymer

( $F_B = 0.80$  and  $F_B = 0.22$ ) in  $\text{CDCl}_3$  are shown in Figures 1 and 2.

In the HSQC spectrum of the poly(*n*-butyl acrylate) the main chain methylene region shows three cross peaks. The meso configuration of the methylene region gives two cross peaks at  $\delta$  35.0/1.90 and 35.0/1.46 ppm because of the two nonequivalent methylene protons. The racemic configuration gives one cross peak in between these two cross peaks at  $\delta$  35.8/1.62 ppm. In the HSQC spectrum of poly(styrene), the SS dyad resonates from  $\delta$  40.5–47/1.2–1.7 ppm.

The methylene carbons in the S/B copolymers are sensitive to compositional sequences. The resonance signals of the methylene carbon region are dyad sensitive. On the basis of variation in intensity of signals with the change in copolymer composition and on comparison with the spectra of poly(*n*-butyl acrylate) and poly(styrene), various dyad compositional sequences in the methylene region are assigned to BB,

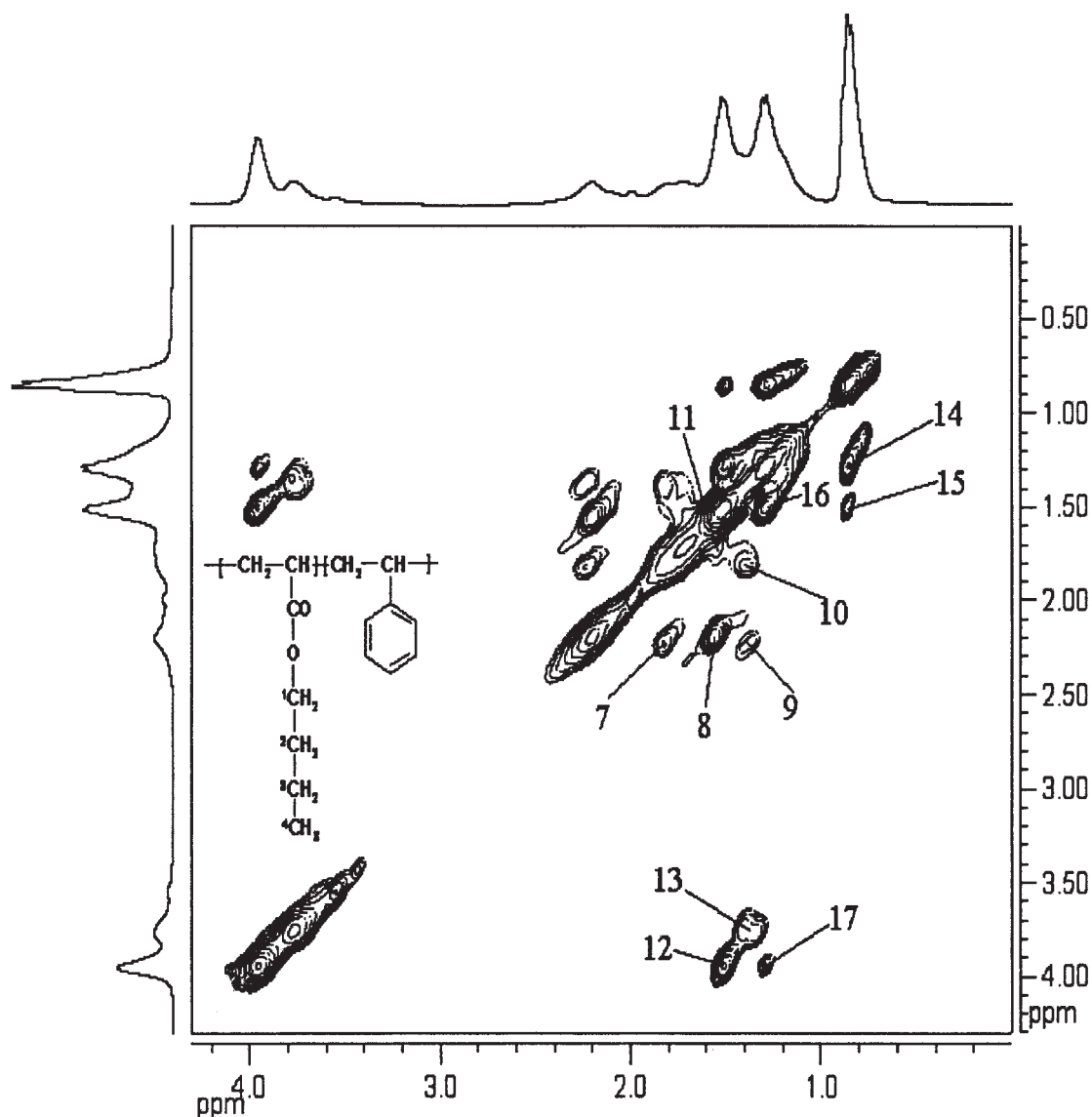


Figure 3 Expanded TOCSY spectrum of S/B copolymer ( $F_B = 0.80$ ) in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

BS, and SS. The BB dyad resonates in the region around  $\delta$  33–37/1.1–1.9 ppm. The two methylene protons of the r dyad are under similar environment, and hence, should give a single cross peak in 2D HSQC NMR spectrum, while the two methylene protons of the B unit in m dyad, being in two different environments, should give two cross peaks in HSQC spectrum. As shown in Figure 1, the cross peak 2 centered at  $\delta$  35.3/1.60 ppm is assigned to the methylene dyad of B unit in racemic (r) configuration (BrB), whereas the cross peaks 1 and 3 centered at  $\delta$  35.2/1.85 and 35.2/1.40 ppm are assigned to the meso (m) configuration (BmB) of the methylene dyad of B unit, respectively. The BS dyad resonates in the region  $\delta$  37–42/1.2–2.1 ppm. The cross peak 4 centered at  $\delta$  39.4/1.78 ppm is assigned to the methylene protons of the BS dyad in meso configuration. Similarly, cross peak 5

centered at  $\delta$  39.4/1.56 ppm is assigned to the methylene protons of the BS dyad in racemic configuration. The SS dyad resonates in the region  $\delta$  42–46/1.4–1.7 ppm. The cross peak 6 (Fig. 2) centered at  $\delta$  44/1.52 ppm is assigned to the SS dyad by comparing with the HSQC spectrum of poly(styrene).

In the HSQC spectrum of poly(*n*-butyl acrylate) and poly(styrene), the methine carbons resonate in the region  $\delta$  39.5–42.5/1.60–2.33 ppm as in the S/B copolymer, therefore, it can not be resolved.

## 2D TOCSY studies

To determine various vicinal and geminal couplings between different protons in the polymer chain, the TOCSY spectra of the copolymers of different compositions, and of poly(styrene) and poly(*n*-butyl acry-

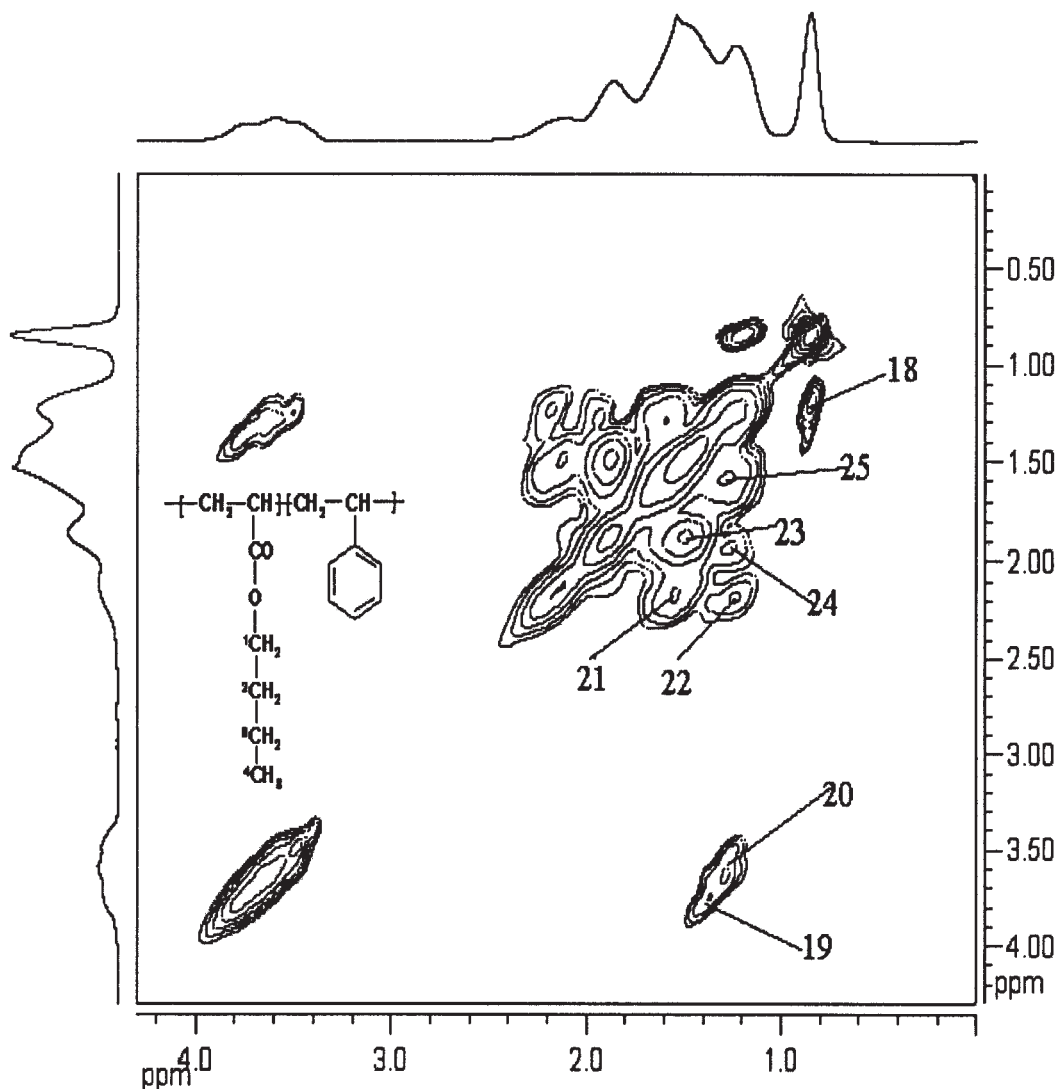


Figure 4 Expanded TOCSY spectrum of S/B copolymer ( $F_B = 0.22$ ) in  $CDCl_3$  at  $25^\circ C$ .

late) are compared. The vicinal couplings between the methine protons in both B and S centered triads with the methylene protons in BB, BS, and SS dyads can be clearly seen in the 2D TOCSY NMR spectrum.

Figure 3 shows the expanded TOCSY spectrum of S/B copolymer ( $F_B = 0.80$ ). In this TOCSY spectrum, three bond coupling between the methylene and methine protons of the BBB unit is observed. The cross peaks 7 and 9 centered at  $\delta$  1.85/2.22 and 1.40/2.22 ppm, respectively, are assigned to coupling between the methylene and methine protons of BBB unit in meso (m) configuration. The cross peak 8 centered at  $\delta$  1.60/2.20 ppm is assigned to coupling between the methylene and methine protons of BBB unit in racemic (r) configuration. The cross peaks 10 and 11 centered at  $\delta$  1.40/1.82 ppm and 1.60/1.80 ppm are due to the overlap of the geminal coupling of the protons of the BBB triad and due to the coupling of methine of the B unit with the methylene protons of styrene in BmBS

and BrBS triad, respectively. On the basis of variation in the composition of the copolymers, and on comparison with the <sup>1</sup>H spectrum of poly (*n*-butyl acrylate), various triad sequences in the <sup>1</sup>OCH<sub>2</sub> region are assigned. The cross peak 12 centered at  $\delta$  1.51/3.95 ppm is assigned to the coupling of <sup>1</sup>OCH<sub>2</sub> with <sup>2</sup>CH<sub>2</sub> in BBB triad. The cross peak 13 centered at  $\delta$  1.40/3.80 ppm is assigned to the coupling of <sup>1</sup>OCH<sub>2</sub> with <sup>2</sup>CH<sub>2</sub> in BBS triad. The cross peaks 14, 15, and 16 centered at  $\delta$  0.86/1.30, 0.86/1.51 and 1.30/1.51 ppm are assigned to the coupling of <sup>4</sup>CH<sub>3</sub> with <sup>3</sup>CH<sub>2</sub>, <sup>4</sup>CH<sub>3</sub> with <sup>2</sup>CH<sub>2</sub>, and of <sup>3</sup>CH<sub>2</sub> with <sup>2</sup>CH<sub>2</sub>, respectively. The cross peak 17 centered at  $\delta$  1.3/3.95 ppm is assigned to the coupling of <sup>1</sup>OCH<sub>2</sub> with <sup>2</sup>CH<sub>2</sub>.

Figure 4 shows the expanded TOCSY spectrum of S/B copolymer ( $F_B = 0.22$ ). The cross peak 18 centered at  $\delta$  0.85/1.19 ppm is assigned to the coupling of the <sup>4</sup>CH<sub>3</sub> with <sup>3</sup>CH<sub>2</sub>. The cross peaks 19 and 20 centered at  $\delta$  1.40/3.78 and 1.28/3.46 ppm are assigned to the

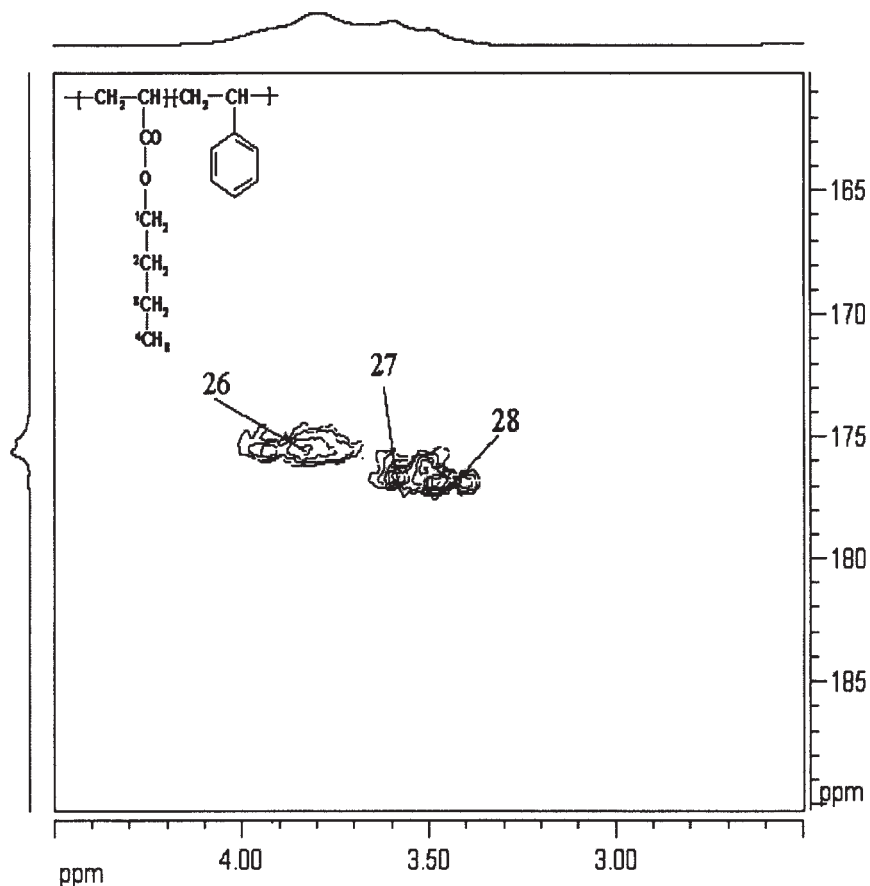


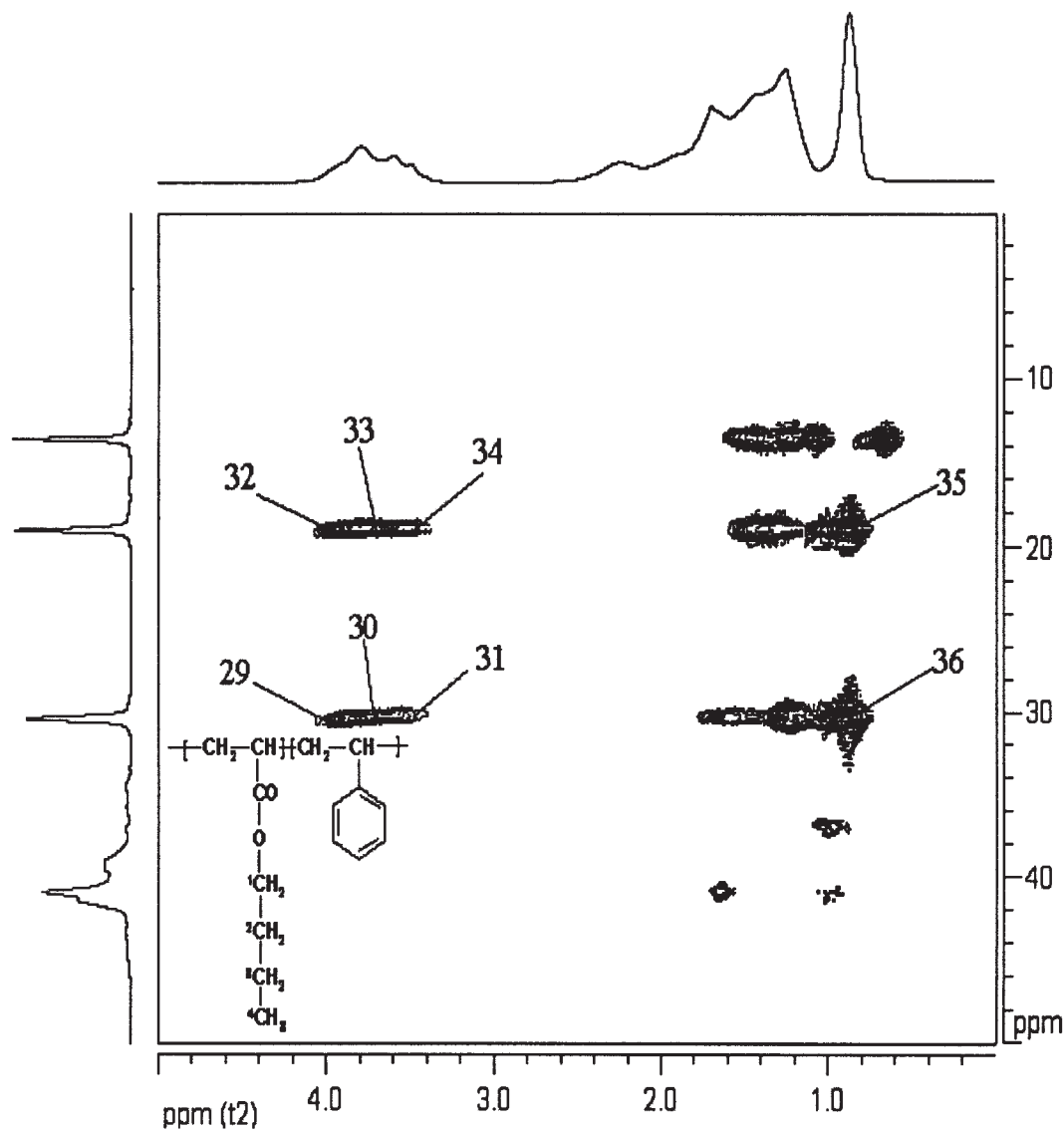
Figure 5 Expanded HMBC spectrum of S/B copolymer showing carbonyl region ( $F_B = 0.54$ ) in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

coupling of  $^1\text{OCH}_2$  with  $^2\text{CH}_2$  and of  $^1\text{OCH}_2$  with  $^2\text{CH}_2$  in BBS and SBS triad, respectively. The cross peak 21 centered at  $\delta$  1.50/2.12 ppm is due to the overlap of coupling of the methine proton of the B unit with the methylene protons of the B unit and also with one of the two different methylene protons of the S unit in SSB triad. The cross peak 22 centered at  $\delta$  1.26/2.12 ppm is due to the coupling of the methine proton of the S unit with one of the two different methylene protons of the S unit in SSB triad in the different environments. The cross peaks 23 and 24 centered at  $\delta$  1.50/1.92 and 1.26/1.94 ppm are due to the geminal coupling of the methylene protons in the SS dyad due to the two different environments in the SSB and SSS triads, respectively. The cross peak 24 is also due to the geminal coupling of the two methylene protons of the B unit. The cross peak 25 centered at  $\delta$  1.26/1.59 ppm is due to the overlap of geminal coupling of the methylene protons in the SS dyad and to the coupling of  $^3\text{CH}_2$  with  $^2\text{CH}_2$  of the B unit.

All these assignments are confirmed by comparing the two-dimensional TOCSY NMR spectra of the copolymers of various compositions to that of the poly(*n*-butyl acrylate) and poly(styrene).

## 2D HMBC studies

HMBC spectrum can be used to study long-range couplings between proton and carbon nuclei. The carbonyl carbon region of the HMBC spectrum of S/B copolymer ( $F_B = 0.54$ ) in  $\text{CDCl}_3$  is shown in Figure 5 along with complete signal assignments. The cross peak 26 centered at  $\delta$  175.86/3.74 ppm is due to the coupling of carbonyl group with BBB of the  $^1\text{OCH}_2$  of the pendant group of the B unit. The cross peaks 27 and 28 centered at  $\delta$  176.96/3.51 and 176.96/3.43 ppm are due to the coupling of the carbonyl group with BBS and SBS of the  $^1\text{OCH}_2$  of the pendant group of the B unit. Figure 6 shows the methylene and methine carbon resonance signals in the expanded HMBC spectrum of S/B copolymer ( $F_B = 0.54$ ) in  $\text{CDCl}_3$ . The cross peaks 29, 30, and 31 centered at  $\delta$  30.3/3.82, 30.3/3.66, and 30.3/3.46 ppm are assigned to the coupling of  $^1\text{OCH}_2$  with  $^2\text{CH}_2$  in the BBB, SBB, and SBS triads, respectively. Similarly, the cross peaks 32, 33, and 34 centered at  $\delta$  18.9/3.82, 18.9/3.66, and 18.9/3.46 ppm are assigned to the coupling of  $^1\text{OCH}_2$  with  $^3\text{CH}_2$  in the BBB, SBB, and SBS triads, respectively. The cross peak 35 centered at  $\delta$  18.9/0.89 ppm is assigned to the coupling of  $^4\text{CH}_3$



**Figure 6** Expanded HMBC spectrum of S/B copolymer showing methylene and methine region ( $F_B = 0.54$ ) in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ .

with  $^3\text{CH}_2$ . Similarly, the cross peak 36 centered at  $\delta$  30.3/0.89 ppm is assigned to the coupling of  $^4\text{CH}_3$  with  $^2\text{CH}_2$ .

### CONCLUSIONS

The overlapped and broad signals in  $^1\text{H}$  and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectra were assigned completely to various compositional sequences, using 2D HSQC, TOCSY, and HMBC experiments. The methylene carbon resonances of B and S unit were assigned to dyad compositional sequences. The unresolved overlapped resonances for the different tacticities of the copolymer in the one-dimensional spectra have been resolved using two-dimensional NMR techniques.

### References

1. Matyjaszewski, K.; Ed. Controlled Radical Polymerization; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998.
2. Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* 1995, 28, 1721.
3. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 1721.
4. Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
5. Nanda, A. K.; Matyjaszewski, K. *Macromolecules* 2003, 36, 1487.
6. Huang, J.; Pintauer, T.; Matyjaszewski, K. *J Polym Sci Part A: Polym Chem* 2004, 42, 3285.
7. Chatterjee, D. P.; Chatterjee, U.; Mandal, B. M. *J Polym Sci Part A: Polym Chem* 2004, 42, 4132.
8. Zhang, H.; Schubert, U. S. *J Polym Sci Part A: Polym Chem* 2004, 42, 4882.
9. Gibson, V. C.; O'Reilly, R. K.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Macromolecules* 2003, 36, 2591.
10. Arehart, S. V.; Matyjaszewski, K. *Macromolecules* 1999, 32, 2221.

11. Karanam, S.; Goosses, H.; Klumperman, B. *Macromolecules* 2003, 36, 3051.
12. Barron, P. F.; Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W. *Macromolecules* 1984, 16, 1967.
13. Randall, J. C. *Polymer Sequence Distribution: Carbon  $^{13}\text{C}$  NMR Method*; Academic Press: New York, 1977.
14. Bovey, F. A.; Mirau, P. A. *NMR of Polymers*; Academic Press: New York, 1996.
15. Matsuzaki, K.; Uryu, T.; Asakura, T. *NMR Spectroscopy and Stereoregularity of Polymers*; Japan Scientific Society: Tokyo, 1996.
16. Hatada, K.; Kitayama, T. *NMR Spectroscopy of Polymers*; Springer-Verlag: Berlin, Germany, 2004.
17. Dutta, K.; Mukherjee, M.; Brar, A. S. *J Polym Sci Part A: Polym Chem* 1999, 15, 551.
18. Asakura, T.; Nakayama, N.; Demura, M.; Asano, A. *Macromolecules* 1992, 25, 4876.
19. Matsuzaki, K.; Uryu, T.; Ishida, A.; Ohki, T.; Takeuchi, M. *J Polym Sci Part A-1: Polym Chem* 1967, 5, 2167.
20. Yoshino, T.; Shinomiya, M.; Komiyama, J. *J Am Chem Soc* 1965, 87, 387.
21. Matsuzaki, K.; Kanai, K. T.; Kawamura, T.; Matsumoto, T.; Uryu, T. *J Polym Sci Polym Chem Ed* 1973, 11, 961.
22. Spyros, A.; Dais, P. *Macromolecules* 1992, 25, 1062.
23. Brar, A. S.; Dutta, K. *Polym J* 1998, 30, 304.
24. Brar, A. S.; Kumar, R.; Kaur, M. *Appl Spectrosc* 2002, 56, 1380.
25. Darricades, M. F.; Pichot, C.; Guillot, J.; Rios, L.; Cruz, M. A.; Guzman, C. *Polymer* 1986, 27, 889.
26. Brar, A. S.; Puneeta. *Indian J Chem Sect A* 2004, 43A, 2281.