

## Characterization of Polyisobutylene–Polybutadiene Diblocks by HMQC and HMBC

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**ABSTRACT:** A combination of NMR experiments was employed to obtain structural information from small numbers of monomer fragments which are at the junctions of the polyisobutylene–polybutadiene diblocks (PIB-*b*-PBD) and to confirm the main chain resonance assignments. The multiplicities of the <sup>13</sup>C resonances were determined using a DEPT experiment, and the one-bond and long-range <sup>1</sup>H/<sup>13</sup>C shift correlations were determined using the indirect detection experiments, HMQC and HMBC, respectively. Previous resonance assignments were based on comparisons with model compounds, correlation of systematic shifts with structural differences, and the APT spectra. The 2D-NMR experiments performed in this work provide definitive proof of the preparation of PIB-*b*-PBD by correlation of resonances of PIB and PBD chain ends with a common structural unit. The chain end resonances of several other structural fragments present in the polymer mixture are also identified.

## Introduction

<sup>1</sup>H-detected heteronuclear multiple-quantum coherence (HMQC)<sup>1,2</sup> and heteronuclear multiple-bond connectivity (HMBC)<sup>3</sup> spectra along with distortionless enhancement by polarization transfer (DEPT)<sup>4</sup> have been used to afford definitive resonance assignments of components in a mixture of products obtained in an attempt to prepare polyisobutylene–polybutadiene diblocks (PIB-*b*-PBD).

HMQC and HMBC have routinely been used in the field of structure determination of biological and small organic molecules because these techniques dramatically enhance the sensitivity of the NMR spectra of nuclei other than protons. By this method, the sensitivity of a nucleus is, in principle, increased by the factor ( $\gamma_H/\gamma_X$ )<sup>3</sup> where  $\gamma_H$  and  $\gamma_X$  are the magnetogyric ratios of <sup>1</sup>H and X nuclei, respectively. For <sup>13</sup>C, the sensitivity is theoretically enhanced 64-fold relative to standard experiments which involve direct detection of <sup>13</sup>C. This sensitivity enhancement is achieved by using *J* couplings to promote coherence transfer from the X nucleus to <sup>1</sup>H followed by detection of the much more sensitive <sup>1</sup>H.

Relatively few applications of inverse detection to structure determination of polymers have been reported in the literature. In some respects, polymers offer much more challenging structural problems than biological macromolecules such as proteins. A major interest of polymer characterization lies in identifying minor structural components and defects. In the specific case of diblock copolymers, many backbone resonances are 2–4 orders of magnitude more intense than the resonances of interest. In contrast, protein NMR involves the suppression of a single water resonance to detect small important resonances whereas in polymer NMR numerous large resonances from the backbone exist and the weaker signals from an important but relatively small number of other structures must be detected in the presence of these large resonances. Furthermore, while proteins are composed of a relatively large number of building blocks with uniform stereochemistry, polymers are prepared with a small number of components with

varying stereochemistry. Consequently, the NMR resonances of polymers tend to be consolidated in relatively small regions, with an equal variety of signals due to numbers of possible stereoisomers. Despite these additional difficulties, techniques which are valuable for biological structure determination can be equally useful for polymer structure characterization.

Well-defined diblock polymers provide interesting opportunities for blending agents of incompatible polymers and controlling material properties. Recently, the preparation of PIB-*b*-PBD has been reported.<sup>5</sup> The polyisobutylene portion was obtained by living cationic polymerization, and the polybutadiene portion, by living anionic polymerization: the starting material, tertiary chloride terminated PIB (PIB-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>Cl, PIB-Cl), undergoes dehydrochlorination–metalation by the *n*-BuLi/*t*-ROK system (R = *tert*-butyl, *tert*-amyl) to yield the PIB-CH<sub>2</sub>C(=CH<sub>2</sub>)CH<sub>2</sub><sup>+</sup> (PIB<sup>+</sup>) anion which induces butadiene polymerization. However, before a detailed investigation into controlling the block lengths can be undertaken, a means of measuring the relative block lengths must be available. The length of the PIB and PBD sequences influences the properties of the block copolymer.

Along with a description of the synthesis of PIB-*b*-PBD, Kennedy *et al.*<sup>5</sup> also reported tentative <sup>1</sup>H and <sup>13</sup>C NMR shift assignments. These assignments were primarily based upon comparison with model compounds, correlation of systematic shifts with structural differences, and attached proton test (APT) experiments to determine the multiplicity of the respective carbons.<sup>6</sup> Very few relevant empirical chemical shift additivity parameters were available and, in addition, this method of assignment is not extremely reliable. Some of the possible products which were anticipated in the preparation of PIB-*b*-PBD are illustrated in Scheme 1, along with <sup>1</sup>H and <sup>13</sup>C spectra shown in Figures 1 and 2, respectively.

The <sup>13</sup>C spectra of the diblock show new resonances in the 51–61 ppm region. The only resonance which appears in this region is the methylene resonance of polyisobutylene. The new signals were assigned as indicated in Scheme 1 and Figure 2 and are thought to arise from methylenes at the junctions between PBD and PIB chain segments.<sup>5</sup> Since the tailored preparation of PIB-*b*-PBD has great potential for a variety of

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Scheme 1

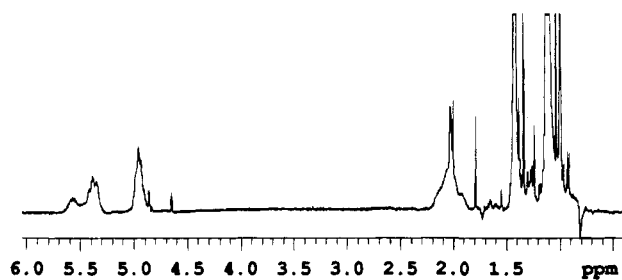
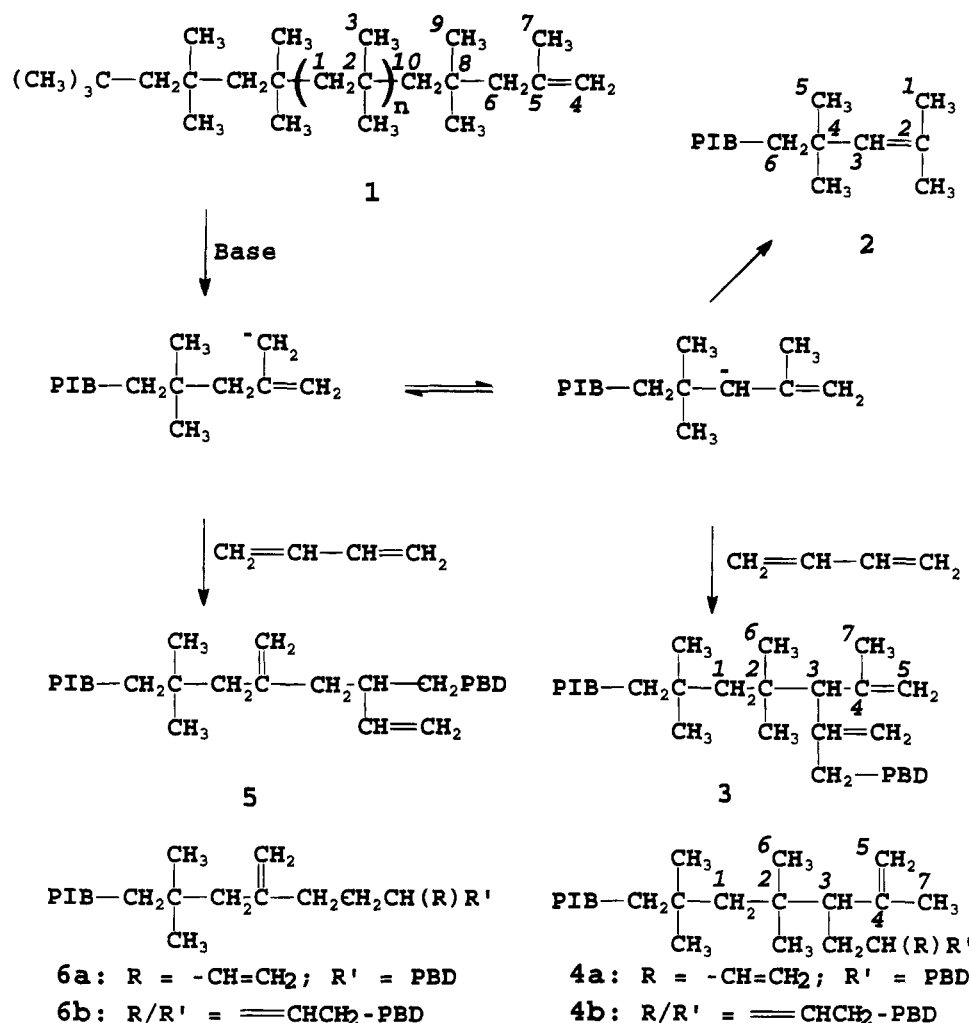


Figure 1. 300 MHz <sup>1</sup>H NMR spectrum of PIB-*b*-PBD in CDCl<sub>3</sub>.

applications, it was worthwhile to obtain complete resonance assignments as a foundation for future work.

### Experimental Section

The sample of PIB-*b*-PBD was provided by Professor J. P. Kennedy; its preparation has been described elsewhere,<sup>5</sup> and it is the same sample used to obtain <sup>1</sup>H and <sup>13</sup>C NMR spectra previously reported.<sup>6</sup> NMR spectra were collected on Varian VXR-300 (with a VXR-4000 data system) and Unity-500 spectrometers. Survey spectra and DEPT spectra were obtained on the VXR-300 instrument and the HMQC and HMBC spectra were obtained on the Unity instrument equipped with a 5 mm indirect detection probe and waveform generator (used to accomplish GARP decoupling in indirect detection experiments). All data were processed with Varian's VNMR software.

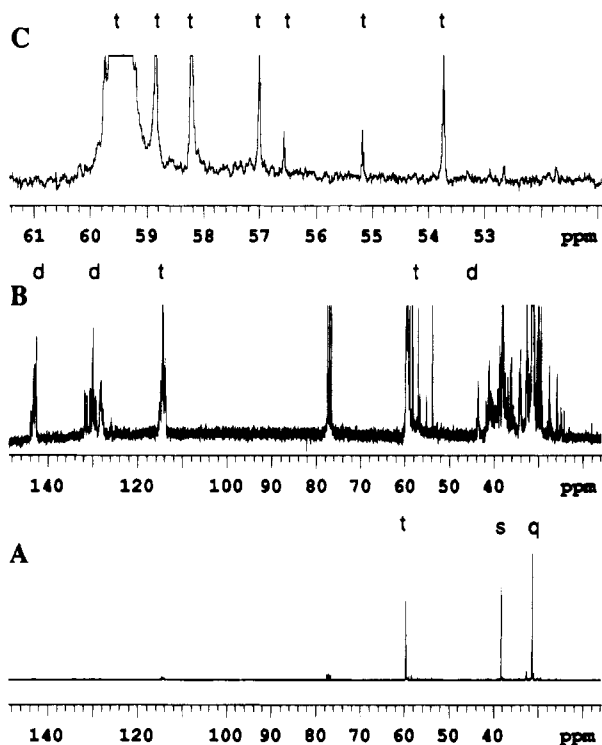
The DEPT spectra were collected at 75.5 MHz on a 150 mg sample in 2.5 mL of CDCl<sub>3</sub>, with a 0.75 s acquisition time (with Waltz decoupling), 15 936 points, a 10 627 Hz spectral window,

a 1.5 s relaxation delay, a 39 μs 90° <sup>1</sup>H pulse, a 18 μs 90° <sup>13</sup>C pulse, and 1024 transients. The data were processed using 1 Hz line broadening and zero filling to 4 times the original data table size.

The <sup>1</sup>H/<sup>13</sup>C heteronuclear shift correlations spectrum was obtained as 75 MHz using a spectral window of 10 040 Hz in *f*<sub>2</sub>, 2048 points, 18 μs 90° <sup>13</sup>C and 39 μs 90° <sup>1</sup>H pulse widths, a 0.102 s acquisition time, and a 1 s repetition rate. A total of 256 spectra (consisting of 64 transients each) were obtained by varying the evolution time between pulses to provide the equivalent of a 1790 Hz spectral window in *f*<sub>1</sub>. The total experiment time was 5.5 h. The data were processed using shifted sine bell weighting and zero filling (2–4 times the original data table size).

The HMQC spectrum was collected at 30 °C on a 10 mg sample in 0.7 mL of CDCl<sub>3</sub> at 499.8 MHz, with a 0.163 s acquisition time (with GARP decoupling), 1024 points, a 3137.7 Hz spectral window in *f*<sub>2</sub>, a 18 854.5 Hz spectral window in *f*<sub>1</sub>, a 1.2 s relaxation delay, a 8.2 μs 90° <sup>1</sup>H pulse, and a 11.0 μs 90° <sup>13</sup>C pulse; 128 dummy cycles were applied followed by averaging 8 transients for each of the 256 complex fid's. The total experiment time was 1.5 h. The data were processed using Gaussian weighting, zero filling (2–4 times the original data table size), the linear prediction in *f*<sub>1</sub> which forward extended the data set 128 complex points using a least-squares calculation of 8 complex *L*<sub>p</sub> coefficients based upon 16 complex time-domain points.<sup>7,8</sup>

The HMBC spectrum was collected at 30 °C on a 10 mg sample in 0.7 mL of CDCl<sub>3</sub> at 499.8 MHz, with a 0.653 s acquisition time (with GARP decoupling), 4096 points, a 3137.7 Hz spectral window in *f*<sub>2</sub>, a 18 854.5 Hz spectral window in *f*<sub>1</sub>, a 1.0 s relaxation delay, a 0.055 s fixed delay which allows for long-range heteronuclear antiphase magnetization to evolve



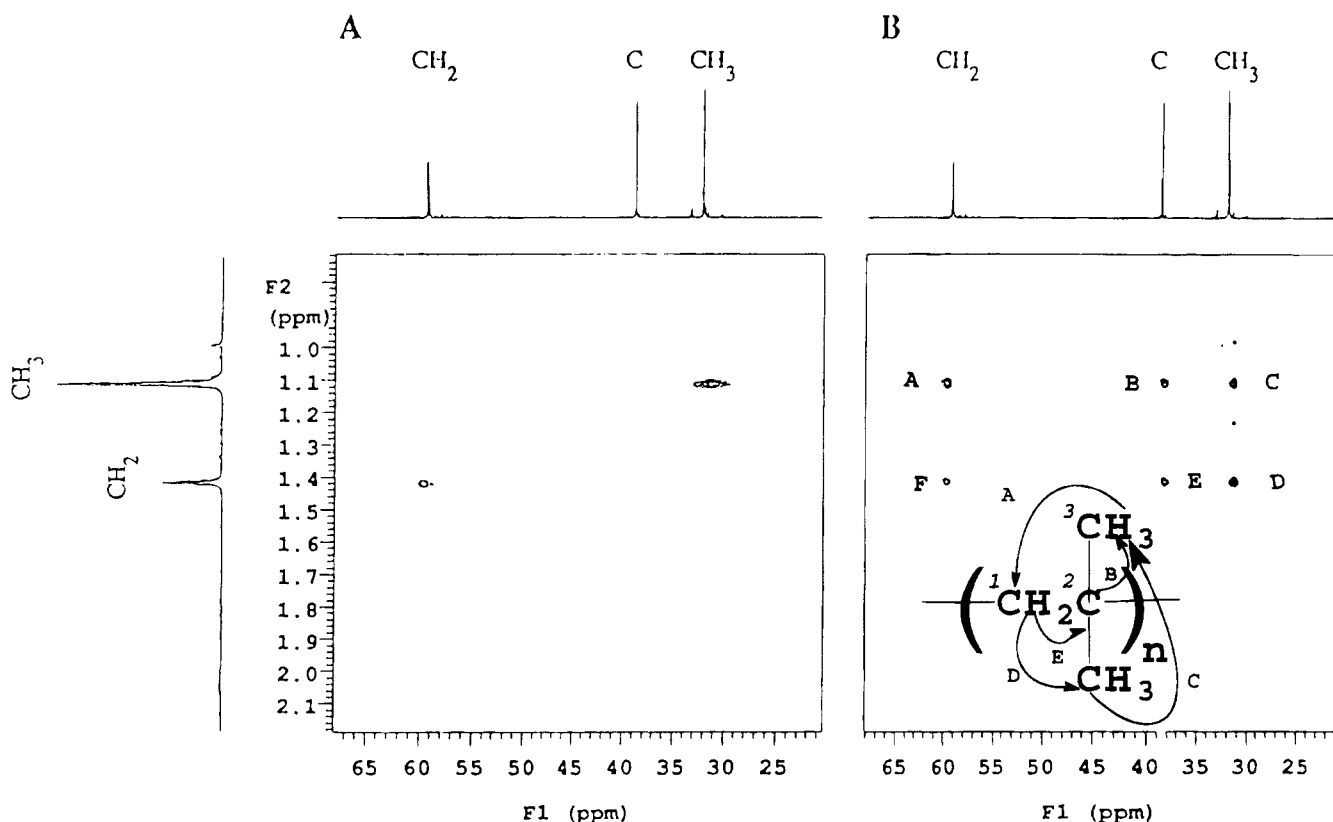
**Figure 2.** 75 MHz  $^{13}\text{C}$  NMR spectrum of PIB-*b*-PBD in  $\text{CDCl}_3$ . Multiplicities indicated (s = C singlet, d = CH doublet, t =  $\text{CH}_2$  triplet, and q =  $\text{CH}_3$  quartet) were obtained from a DEPT experiment at 75 MHz. (A) The Full  $^{13}\text{C}$  spectrum (from left to right) shows the  $\text{CH}_2$ , C, and  $\text{CH}_3$  signals of the PIB main chain. (B) A 100-fold vertical expansion reveals numerous resonances from different chain end and block juncture structures. (C) A vertical expansion of the  $\text{CH}_2$  region which contains the new resonances obtained by the blocking of the PBD segment from PIB $^-$ .

for multiple-bond correlation, a  $8.2\ \mu\text{s}\ 90^\circ\ ^1\text{H}$  pulse, and a  $11.0\ \mu\text{s}\ 90^\circ\ ^{13}\text{C}$  pulse; 128 dummy cycles were applied followed by averaging 64 transients for each of the 280 complex fid's. The total experiment time was 15.5 h. The data were processed using shifted sine bell weighting, zero filling (2–4 times the original data table size), and linear prediction in *f1* which forward extended the data set 128 complex points using a least-squares calculation of 16 complex *Lp* coefficients based upon 32 complex time-domain points.<sup>7,8</sup>

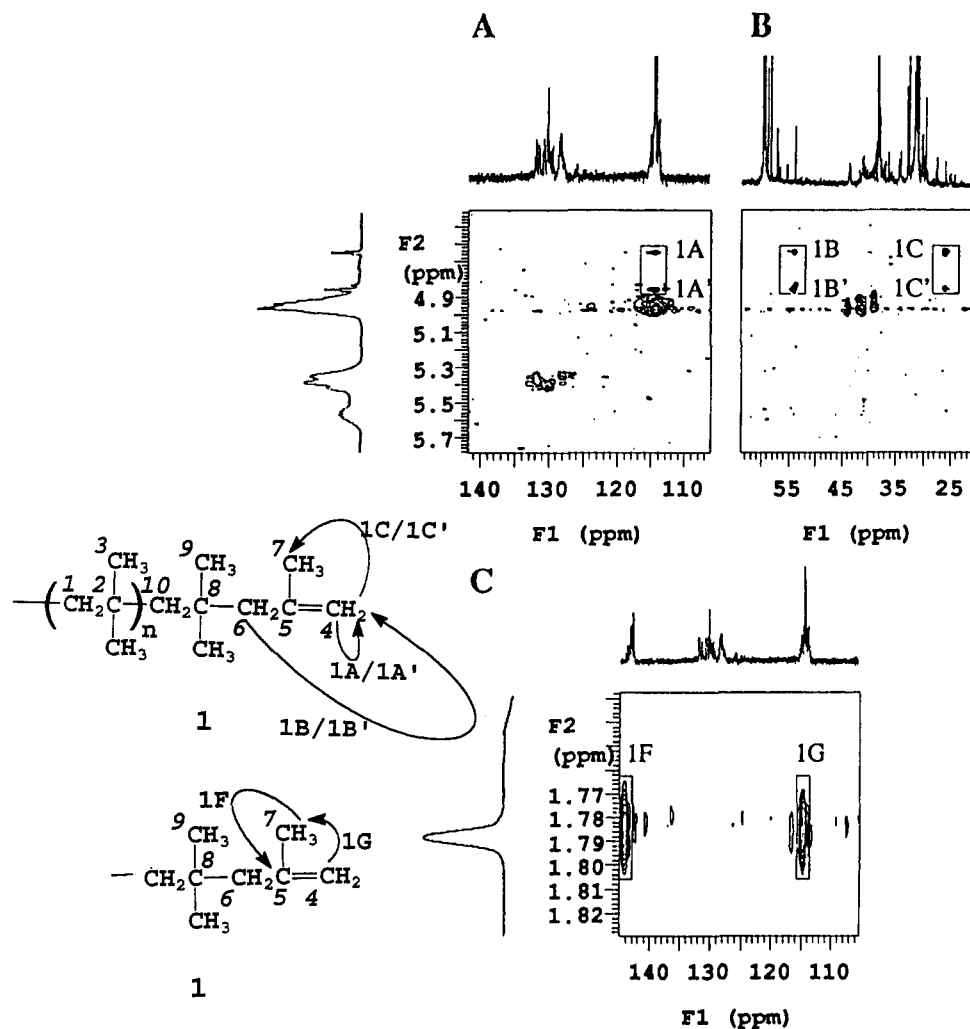
## Results and Discussion

**$^1\text{H}$  NMR.** The  $^1\text{H}$  NMR spectrum of the PIB-*b*-PBD sample is shown in Figure 1. The resonances in the aliphatic region (1.0–2.5 ppm) overlap severely. Two intense singlets at 1.1 and 1.4 ppm result from the PIB backbone. The aliphatic resonances at ca. 2 ppm are derived from the PBD backbone and arise from  $\text{CH}$ 's of repeat units formed by 1,2-addition and  $\text{CH}_2$ 's of repeat units formed by 1,4-addition. The olefin resonances between 5.0 and 5.6 also are derived from the PBD backbone and arise from  $-\text{CH}=\text{CH}_2$  fragments of repeat units formed by 1,2-addition and  $=\text{CH}-$  fragments of repeat units formed by 1,4-addition. A comparison of the relative intensities of aliphatic of olefin regions indicates an 80/20 ratio of PIB/PBD. However, these spectra alone do not provide evidence that these components are part of the same polymer chain.

The  $^{13}\text{C}$  NMR spectrum of the mixture obtained from the preparation of the PIB-*b*-PBD sample is shown in Figure 2. The main chain resonances of PIB, Figure 2A, are very intense and were identified by a DEPT experiment: C, 38.15 ppm;  $\text{CH}_2$ , 59.5 ppm;  $\text{CH}_3$ , 31.3 ppm. A 100-fold vertical scale expansion of the  $^{13}\text{C}$  spectrum, Figure 2B, reveals numerous resonances from different chain end and block juncture structures. Of particular interest were the unique  $\text{CH}_2$  resonances from different products in the final mixture whose multiplicities were identified through a DEPT experi-



**Figure 3.** 500 MHz HMQC (A) and HMBC (B) spectra of PIB-*b*-PBD diblock polymer showing the correlations of the main PIB backbone resonances.



**Figure 4.** (A) Expansion from the 500 MHz HMQC spectrum of PIB-*b*-PBD diblock polymer showing correlations between olefin carbons and olefin protons. (B) and (C) Expansions from the 500 MHz HMBC of PIB-*b*-PBD diblock polymer showing correlations between olefin protons and aliphatic carbons and an aliphatic proton and olefin carbons, respectively. The correlations are numbered accordingly to show the stepwise tracing of the resonance assignments from starting material 1.

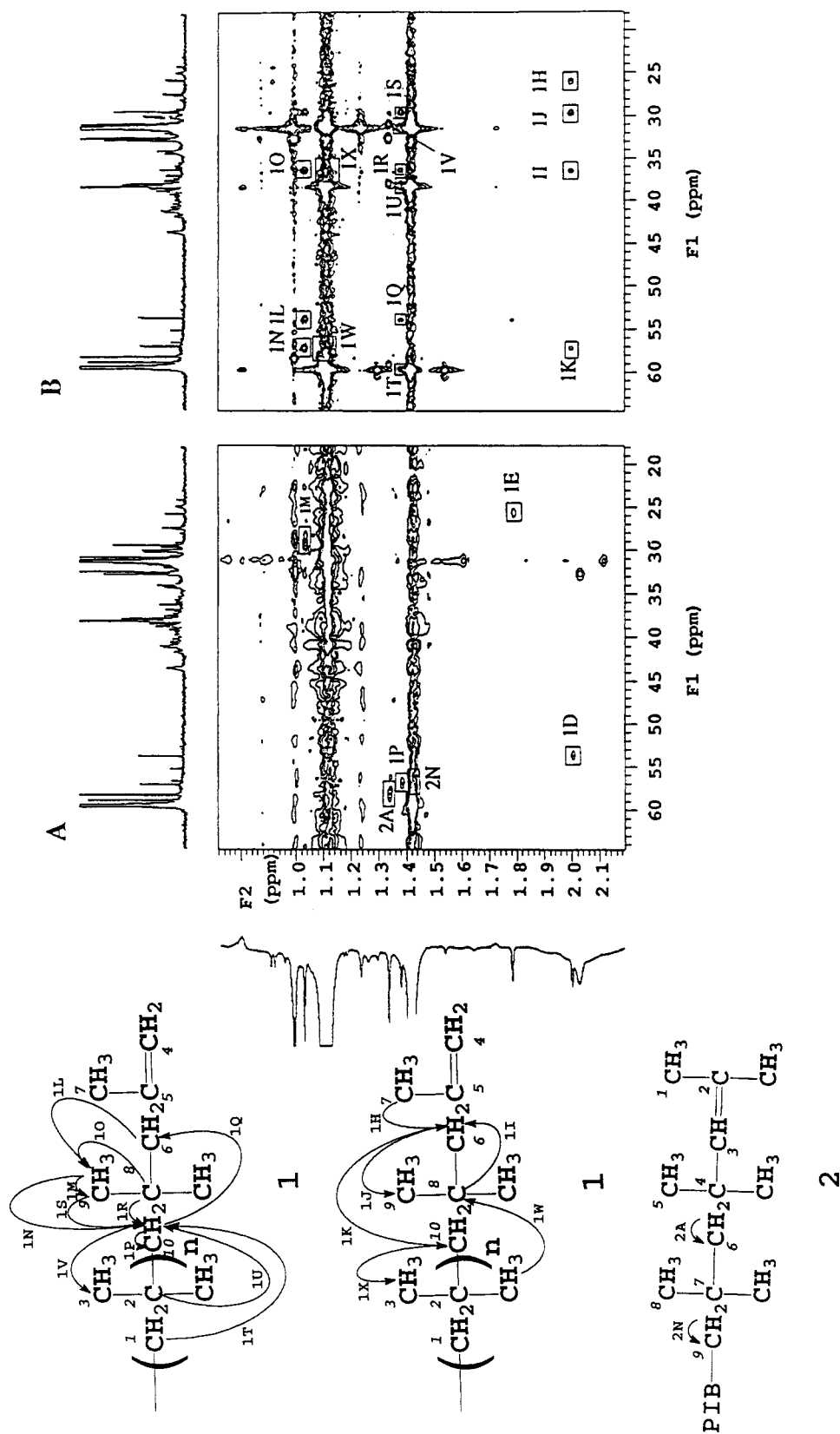
ment, a portion of which is presented in Figure 2C. These signals, especially the CH<sub>2</sub> resonances in the 50–60 ppm region, provide an excellent means of monitoring the ratio of components and also provide a common ground for determining the structure of various products since most of the other resonances can be related via 2D-NMR to one of these signals. These CH<sub>2</sub> resonances will eventually provide a means of monitoring the presence of various products which are possible in these block copolymerizations.

**HMQC and HMBC of PIB Backbone.** Tracing the atomic connectivities in the main chain repeat units of the PIB backbone (structure 1) serves as a simple example of applying HMQC to identify correlations from one-bond CH couplings and HMBC to identify correlations from long-range CH couplings. The HMQC spectrum shows the backbone methyl resonance at 31.3 ppm is coupled to directly bound protons with resonances at 1.12 ppm, and the methylene carbon resonance at 59.5 ppm is coupled to directly bound protons with resonances at 1.4 ppm, Figure 3A. In the HMBC spectrum, Figure 3B, the methyl protons show long-range couplings to a quaternary carbon (38.15 ppm) and a methylene carbon (59.5 ppm) (crosspeaks B and C, respectively). In addition, the methylene protons with a resonance at 1.42 ppm exhibit long-range coupling to the methyl and quaternary carbons (crosspeaks D and E, respectively). Thus, the resonances of the backbone

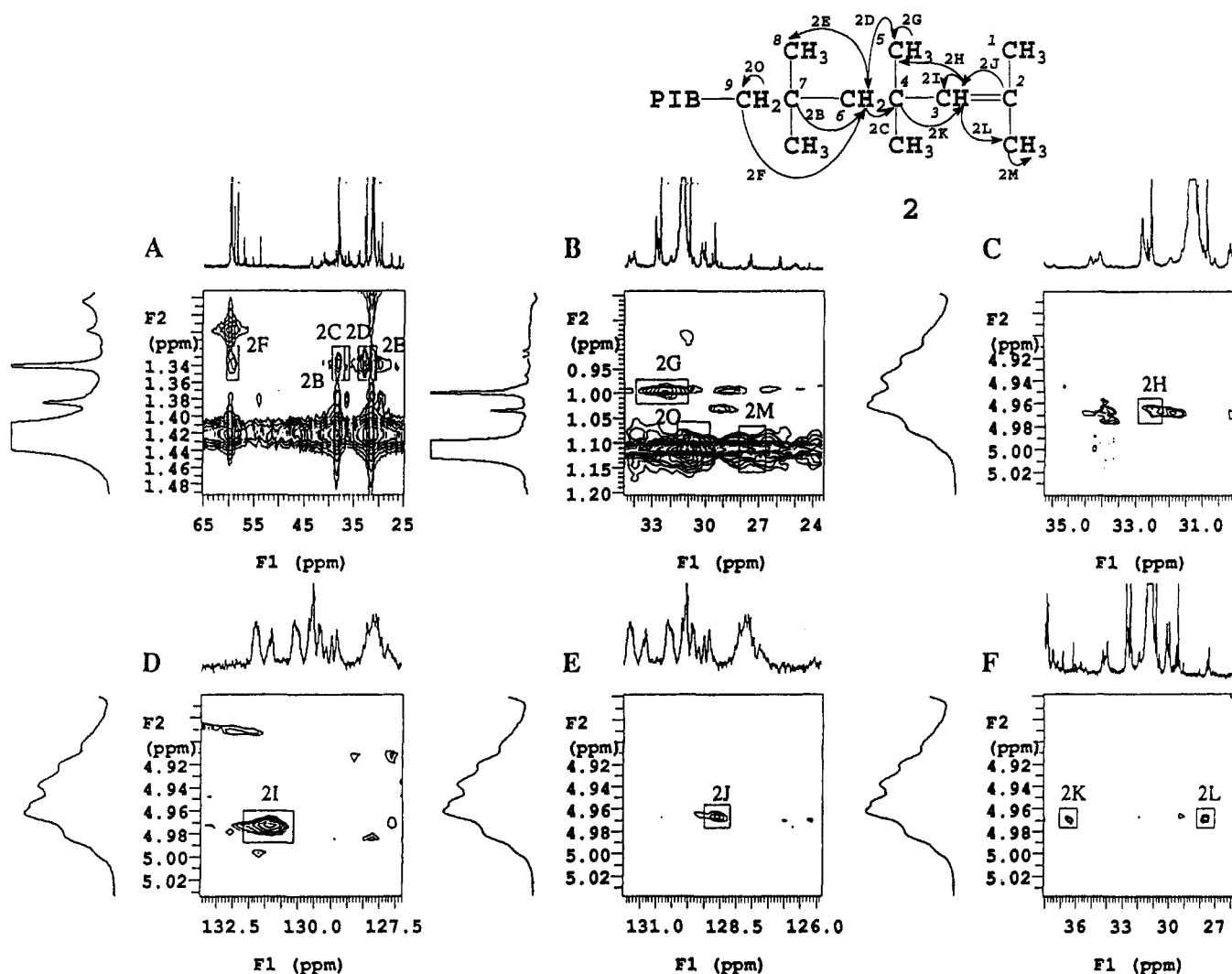
are easily mapped. Note that HMBC crosspeaks are also found between the methyl protons and the geminal methyl carbon (crosspeak C) and between the methylene protons and the methylene carbons on the adjacent repeat units in the polymer chain (crosspeak F). Additionally, "leakage" of HMQC crosspeaks can often be seen in HMBC spectra; an example is the doublet (with  $^1J_{CH} = 130$  Hz in  $f_2$ ) which flanks crosspeak C in Figure 3B.

Similar assignments have been obtained at 300 MHz. The region between 51 and 61 ppm contained only methylene carbons. The PIB repeat units were easily confirmed at 300 MHz using conventional heteronuclear chemical shift correlation experiments<sup>9–11</sup> and correlated spectroscopy for long-range coupling (COLOC)<sup>12,13</sup> experiments which involved <sup>13</sup>C detection. However, very little information on the microstructure of the diblock could be obtained from these experiments due to inadequate sensitivity which prevented the detection of weak signals from small amounts of these structures in polymers. However, the HMQC and HMBC experiments performed at 500 MHz successfully provided definitive structure assignments for not only the backbone, as shown from the interpretation of the spectra in Figure 3, but also other structural units.

**HMQC and HMBC Structure 1.** If one increases the vertical scale by 2<sup>5</sup>–2<sup>8</sup> compared with the contour plots from the HMQC and HMBC spectra showing the



**Figure 5.** Expansions from the 500 MHz HMQC (A) and HMBC (B) spectra showing correlations between aliphatic protons and aliphatic carbons. Correlations assist in assigning the resonances from structures 1 and 2.



**Figure 6.** Expansions from the 500 MHz HMQC (B and D) and HMBC (A, C, E, and F) spectra illustrating many of the resonance assignments for an alternative polyisobutylene end group, structure 2.

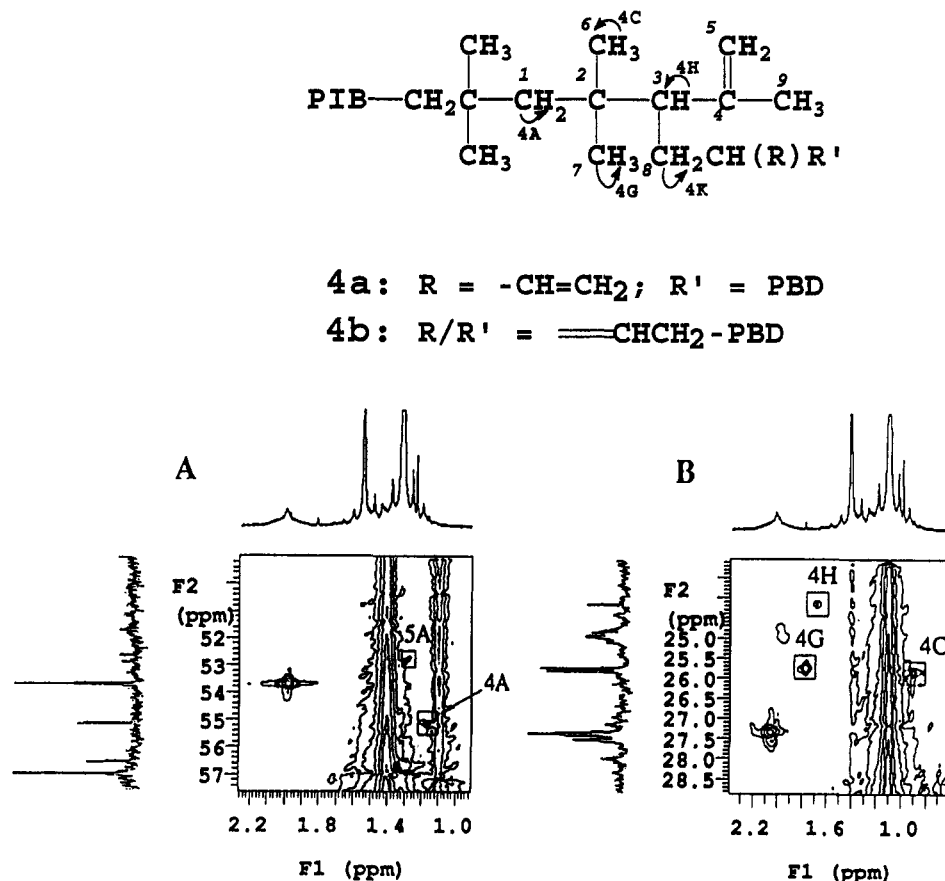
backbone signals, Figure 3, the crosspeaks from numerous other structural fragments are evident. The resonances from the unsaturated chain end of starting material 1 can be unambiguously assigned using the HMQC and HMBC spectra. All atom numbers in this section refer to structure 1 in Scheme 1. The two geminal protons at 4.65 and 4.86 ppm, H-4 and H-4', are correlated with the directly bound carbon resonance at 114.5 ppm (Figure 4A, correlation 1A and 1A'). These olefin protons also show long-range coupling to a methylene carbon, 54.03 ppm, and a methyl carbon, 26.0 ppm (Figure 4B, correlations 1B, 1B' and 1C, 1C'). Crosspeaks 1D and 1E from protons with resonances at 2.0 and 1.79 ppm, respectively, in the HMQC spectrum (Figure 5A) are correlated with these carbons and must be H-6 methylene and H-7 methyl resonances, respectively. The methyl protons, H-7, have long-range coupling to a quaternary carbon, C-5, at 144.2 ppm (Figure 4C, correlation 1F); thus, the assignment of the terminal group is complete.

Previously established resonance assignments can be verified by examining the long-range couplings which are present between some of the other proton and carbon resonances in structure 1. For example, crosspeak 1G (Figure 4C) indicates long-range coupling between H-7 and C-4. The methylene protons H-6 have long-range coupling to C-7, C-8, and C-9 (Figure 5B, correlations 1H, 1I, and 1J). Furthermore, a weak correlation is also present between H-6 and C-10 (Figure

5B, correlation 1K), while the methylene carbon C-6 (54.03 ppm) exhibits long-range coupling with H-9 at 1.03 ppm (Figure 5B, correlation 1L). Moving to H-9, a correlation through one-bond coupling is present to C-9 ( $\delta = 29.4$  ppm, Figure 5A, correlation 1M). In addition, the methyl protons H-9 have a long-range coupling to another methylene, C-10, at 57.0 ppm, and a quaternary carbon C-8 at 36.4 ppm (Figure 5B, correlations 1N and 1O). Carbon C-10 is directly coupled to protons at 1.38 ppm (Figure 5A, correlation 1P), establishing the latter as methylene signals H-10.

An examination of the long-range couplings of methylene protons H-10 affords resonance assignments for structure 1 which are first internally consistent with the assignments described above and second establish the connection between this polyisobutylene end group and the main chain backbone. The correlations 1Q, 1R, and 1S, Figure 5B, between H-10 and C-6, C-8, and C-9, respectively, reaffirm the resonance assignments previously proposed for structure 1. Furthermore, correlations 1T, 1U, and 1V in Figure 5B are present due to long-range coupling between the H-10 methylene protons and C-1 (59.5 ppm), C-2 (38.15 ppm), and C-3 (31.3 ppm), respectively. These carbon resonances are those of the main chain repeat units of PIB.

Lastly, both the quaternary carbon C-8 and the methylene carbon C-10 exhibit crosspeaks due to long-range coupling to the methyl protons H-3 at 1.12 ppm which compose part of the PIB backbone (Figure 5B,



**Figure 7.**  $\{^1\text{H}\}^{13}\text{C}$  heteronuclear shift correlation spectrum obtained at 75 MHz. From (A) two key one-bond correlations are established between methylene carbons in structures 4 which appear due to the blocking of the PBD segment from PIB<sup>-</sup> and their respective directly bound protons. (B) illustrates additional one-bond couplings of resonances in structure 4.

correlation 1W and 1X). Thus, the resonance assignments for the terminal end group of PIB (structure 1) are complete and internally consistent, and its connection to the main chain backbone is shown.

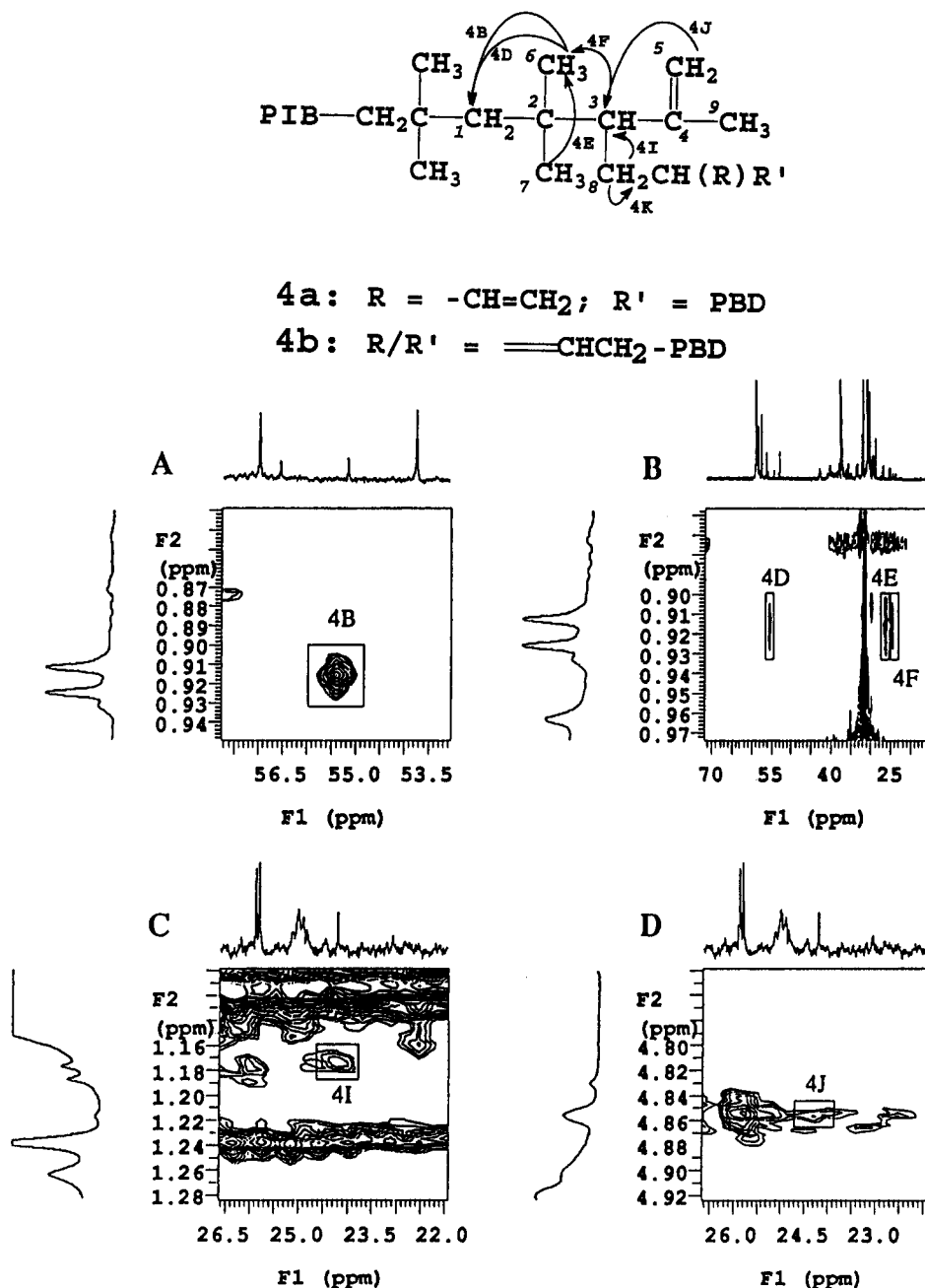
**HMQC and HMBC Structure 2.** The resonances from an alternative PIB end group can also be identified from the combination of HMQC and HMBC data in hand. The identification of each group provides valuable spectroscopic information which can be used in ongoing investigations directed toward the synthesis and identification of end-functionalized PIBs. Atom numbers in this section refer to structure 2 in Scheme 1.

The initial identification of the methylene C-6 at 58.2 ppm proved to be the key in solving the resonance assignments for structure 2. According to the HMQC spectrum, the directly bound protons H-6 are at 1.32 ppm (Figure 5A, correlation 2A). In Figure 6A, crosspeaks are evident due to long-range couplings between H-6 and five carbons: two methyl carbons at 32.5 and 30.8 ppm (correlations 2D and 2E); two quaternary carbons at 36.4 and 37.8 ppm (correlations 2B and 2C); a methylene carbon at 58.5 ppm (correlation 2F). The structure can be assembled by starting with the methyl carbon resonance (C-5) at 32.5 ppm; it is coupled to directly bound protons (H-5) at 1.0 ppm (correlation 2G in the HMQC spectrum, Figure 6B) and has long-range coupling to an olefin proton (H-3) at 4.96 ppm (Figure 6C, correlation 2H). From the HMQC spectrum, the olefin proton H-3 is proven to be directly bound to a methine carbon at 132 ppm (Figure 6D, correlation 2I). Crosspeaks are observed from long-range couplings between H-3 and a nonprotonated olefin carbon (128 ppm), a quaternary carbon (37.8 ppm), and a methyl

carbon (28.7 ppm) (Figure 6E,F, correlations 2J, 2K, and 2L, respectively). The quaternary carbon at 128.0 is C-2, while the methyl carbon at 28.7 ppm must be C-1. Lastly, the quaternary carbon at 37.8 ppm was the same carbon which exhibited long-range coupling to methylene protons H-6 and therefore must be C-4. To complete the proton assignments, correlation 2M relates the methyl carbon C-1 at 28.7 ppm to protons at 1.1 ppm in the HMQC spectrum, Figure 6B.

Returning to the other unidentified carbons which exhibit long-range coupling to H-6, we have a quaternary (36.4 ppm), a methyl (30.8 ppm), and a methylene carbon (58.8 ppm) which should form a PIB structural unit corresponding to carbons C-7, C-8, and C-9, respectively. These carbon resonances are still slightly shifted from the resonances of the main chain backbone due to their proximity to the isobutylene chain end; however, the directly bound protons H-8 and H-9 are at the same resonance frequencies as the main chain backbone methylene and methyl protons at 1.42 and 1.12 ppm, respectively (Figures 5A and 6B, correlations 2N and 2O).

**HMQC and HMBC Structure 4.** Nemes and Kennedy<sup>5</sup> predicted the chemical shifts of the four new methylene carbon resonances on the basis of the expected microstructures of the first BD unit attached to PIB, as shown in Scheme 1, structures 3–6. Complete resonance assignments for these fragments are not available from the data in hand due to the relatively small amount of these components in the mixture. However, the HMQC and HMBC spectra provide assignments of the resonances which are consistent with the presence of 4.



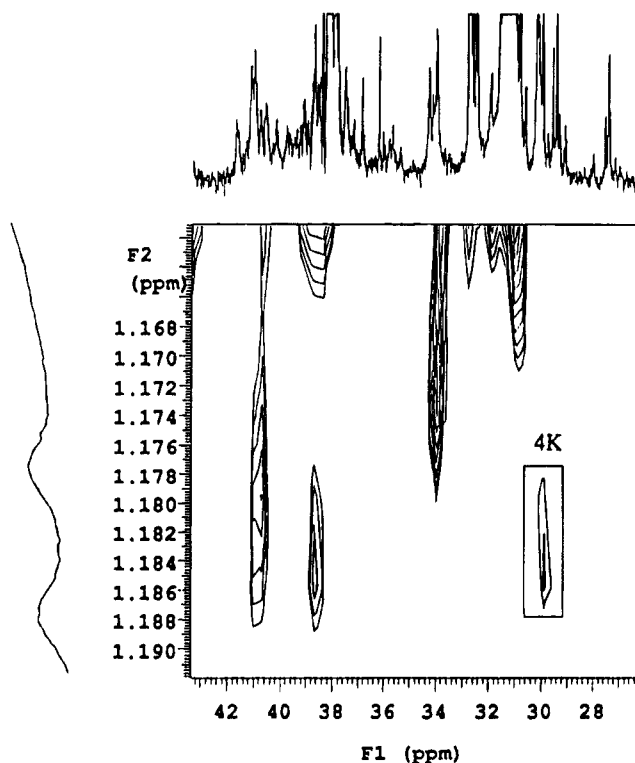
**Figure 8.** Expansions from the 500 MHz HMBC spectrum which show key long range couplings necessary to definitively prove the juncture between PIB and PBD in structure 4.

All atom numbers in this paragraph refer to structure 4 in Scheme 1 unless otherwise stated. According to the DEPT spectra, the carbon at 55.3 ppm is a methylene carbon. It is coupled to directly bound protons at 1.24 ppm (Figure 7A, correlation 4A, C-1/H-1). Long-range coupling is present between the C-1 resonance and the proton resonance at 0.92 ppm (Figure 8A, correlation 4B). The proton resonance at 0.92 is known to be from a methyl group because it shows a crosspeak from one-bond C-H coupling (Figure 7B, correlation 4C) to a methyl carbon resonance at 25.86 ppm (identified from a DEPT spectrum). Crosspeaks 4D, 4E, and 4F (Figure 8B) relate this same methyl proton resonance to three carbon resonances at 55.3, 25.79, and 24.26 ppm, respectively. The methylene resonance at 55.3 ppm has already been assigned to C-1. The methyl carbon with resonance at 25.79 ppm has directly bound protons with a resonance at 1.79 ppm (Figure 7B, correlation 4G) and can be assigned to C-7. The final carbon resonance at 24.26 ppm has one-bond coupling

to a proton at 1.65 ppm (Figure 7B, correlation 4H). The DEPT spectrum shows that this carbon arises from a methine group, even though it is shifted upfield substantially, and therefore can be assigned to C-3. Protons exhibiting long-range couplings to C-3 include those with resonances at 1.18 and 4.86 ppm (Figure 8C,D, correlations 4I and 4J). The aliphatic protons at 1.18 ppm are directly attached to methylene carbon C-8 at 29.84 ppm (Figure 9, correlation 4K). The olefin protons at 4.86 ppm are part of the same structural unit as previously discussed and have chemical shifts similar to those of the terminal olefin connected to an isobutylene unit of a PIB, structure 1, C-4. In structure 4, the resonances at ca. 4.86 ppm are attributed to H-5. Further assignments of C-4, C-7, and C-2 cannot be made with the data in hand. However, we have unequivocally established the juncture between the blocks.

A summary of resonance assignments for structures 1, 2, and 4 are presented in Table 1. Although reso-





**Figure 9.** Expansion from the 500 MHz HMQC spectrum showing the connection between aliphatic protons and a methylene carbon in structure 4.

nances can be identified which are consistent with the presence of additional structures in Scheme 1, complete assignments for these additional structures cannot be made with the data at hand. Artifacts from imperfect cancelation of undesired signals components, which are characteristic of HMBC spectra, create noise ridges which interfere with the detection of many of the signals necessary for their complete structure determinations.

## Conclusion

In conclusion, by following direct and long-range C–H couplings in the HMQC and HMBC spectra, respectively, it is possible to trace the atomic connectivities of various structural fragments in diblock copolymers. In the case of PIB-*b*-PBD, we were able to offer definitive proof that some PIB and PBD units are part of the same polymer chain. This information could not be obtained from previous spectroscopic studies. The initial assignments by Nemes and Kennedy<sup>5</sup> of the four new methylene carbon resonances based upon the expected microstructure of the first BD unit attached to PIB as shown in Scheme 1 were indeed correct, and resonances from a new structure arising from rearrangement of the PIB chain end are identified. These assignments provide vital information about the detailed termination chemistry of polymerizations. Also, they offer valuable insights into the mechanism by which molecular weights

**Table 1.** Compilation of  $^{13}\text{C}$  and  $^1\text{H}$  Chemical Shift Assignments for Structures 1, 2, and 4

structure	carbon	multiplicity <sup>a</sup>	$^{13}\text{C}$ (ppm)	$^1\text{H}$ (ppm)
1	1	t	59.5	1.42
	2	s	38.15	
	3	q	31.3	1.12
	4	t	114.5	4.65 and 4.86
	5	s	144.2	
	6	q	26.0	1.79
	7	t	54.03	2.0
	8	s	36.4	
2	9	q	29.4	1.03
	1	q	28.7	1.10
	2	s	128.0	
	3	d	132	4.96
	4	s	37.8	
	5	q	32.5	1.0
	6	t	58.2	1.32
	7	s	36.4	
4	8	q	30.8	1.12
	9	q	58.5	1.42
	1	t	55.3	1.24
	3	d	24.6	1.65
	5	t		4.86
	6	q	25.86	0.92
	7	q	25.79	1.79
	8	t	29.84	1.18

<sup>a</sup> From DEPT experiment: s = C, d = CH, t = CH<sub>2</sub>, and q = CH<sub>3</sub>.

can be controlled since the block lengths in copolymers determine polymer properties.

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