Monomer Sequence Distributions in Propylene−1-Butene Random Copolymers

Yu-Dong Zhang†

Beijing Research Institute of Chemical Industry, SINOPEC, 100013, Beijing, PR China

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ABSTRACT: A new carbon-13 NMR method is presented for the quantitative determination of monomer sequence distributions and average sequence lengths in propylene−1-butene copolymers. Complete carbon-13 NMR chemical shift assignment was finalized: the peaks corresponding to comonomeric sequence distributions are assigned in terms of previous assignments, and other peaks are formulated after observation of two reference systems: a propylene homopolymer and a propylene copolymer with 8.17 mol % 1-butene. Particular attention was focused on determination of the P-centered triad sequence distributions, and the monomer sequence distributions were quantitatively determined, based directly on either the isolated carbon-13 NMR peaks or on the sequence distribution relationship equations. In addition, the effect of the propylene sequence configuration on the quantitative determination of the monomer sequence distributions of PP-centered tetrads was minimized. Molecular microstructural information was extracted with the highest possible accuracy. This method is reliable for analysis of the monomer sequence distributions in propylene−1-butene random copolymer.

Introduction

Propylene−1-butene copolymers, unlike ethylene−propylene copolymers and ethylene−1-butene copolymers, have received relatively less attention in carbon-13 NMR studies, even though over 20 years ago the carbon-13 NMR technique was utilized to characterize their molecular microstructure and to determine the monomer sequence distributions.[1−9] The studies of Randall, Cheng, and Aoki are considered the most significant in this field:[3,6−8] they determined the chemical shift assignments of triad and tetrad sequences from chemical shift calculations using empirical rules and comparison of the spectra of copolymers with different compositions.[3,4] In addition, the pentad and hexad sequence assignments were proposed from quantitative analysis of the spectrum by a reaction probability model.[6] Aoki et al. advanced the study in this field:[7,8] use of the powerful 2D-INADEQUATE technique determined the carbon-13 NMR chemical shift assignments in propylene−1-butene copolymers and confirmed the validity of previous assignments of triad and tetrad sequences.[6] Furthermore, to predict the fine chemical shift assignments of hexad or pentad sequences by chemical shift calculation via the carbon-13 NMR γ effect, Mark's modified[10] rotational isomeric state model (RIS model) is used, in which side-chain conformation in a 1-butene unit is considered in calculating chemical shift. Therefore, the chemical shift assignments of hexad or heptad monomer sequences have been finalized in a propylene−1-butene copolymer. However, factors such as configuration of propylene sequence, serious overlap of peaks between configurational sequence distributions and comonomeric sequence distributions, as well as longer spin−lattice delay time, T_1, of methyl carbon, were not considered at all. Undoubtedly, there are as yet some unresolved important questions. For example, the monomer sequence distributions in propylene copolymers with comparatively small amounts of 1-butene cannot be accurately determined by the above-mentioned method, in particular, the P-centered triad sequence distributions. As we know from the previous assignments,[3,6−8,11] propylene−1-butene copolymers have comparatively less comonomeric sequence sensitivity than configurational sequence sensitivity, and these serious peak overlaps must result in error in calculation of the monomer sequence distributions, particularly those propylene copolymers with comparatively small amounts of 1-butene. In addition, longer spin−lattice delay time, T_1, of methyl carbon also affects the accuracy of the determination.[12] Thus, it is necessary to determine the monomer sequence distributions in propylene−1-butene copolymer by use of a new method.

The aim of this paper is to introduce a new method for accurately determining the sequence distributions: to characterize the molecular microstructure of propylene copolymers with small amounts of 1-butene by use of a 100 MHz high-field carbon-13 NMR spectrometer, and to determine the virgin monomer sequence distributions by minimization of the effect of the above-mentioned factors, such as configuration of the propylene sequence. First, the chemical shift assignments of the propylene−1-butene copolymer are finalized as follows. The peaks corresponding to comonomeric sequence distributions are assigned in terms of the previous assignments,[3,6−8] and the other peaks are formulated after observation of two reference systems: a propylene homopolymer and a propylene copolymer with 8.17 mol % 1-butene comonomer, on the basis of the chemical shift assignments in relationship to configurational distributions of propylene sequence from Busico.[11] Subsequently, the virgin monomer sequence distributions of the copolymer are determined with the highest possible accuracy by minimizing a series of errors resulting from calculation and the above-mentioned factors. It is worth noting that first, some sequence distribution relationship equations are used in the new method to determine certain sequence distributions, for example, the important P-centered

† Present address: School of Electronics and Computer Science, University of Southampton, U.K. E-mail: yz@ecs.soton.ac.uk. Permanent e-mail: doctorydzhang@yahoo.com.cn.

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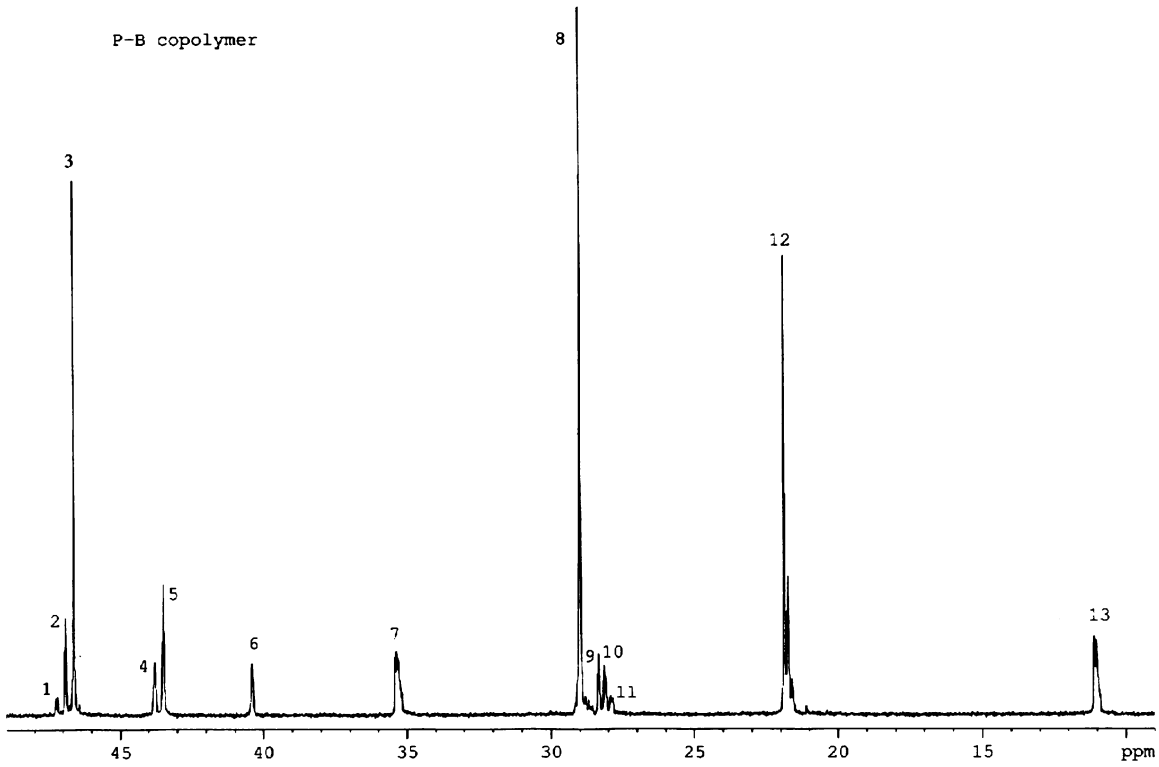

Figure 1. Carbon-13 NMR spectrum of a propylene copolymer with 8.17 mol % 1-butene recorded on a Bruker Avance DMX 400 MHz spectrometer operated at 100 MHz at 125 °C.

triad sequence distributions, and second, only peaks arising from methylene, methine carbons, and no methyl are employed in the quantitative determination of monomer sequence distributions, taking into consideration longer spin−lattice delay time, T_1, of the methyl carbons.

Experimental Section

Materials. A set of propylene copolymers with 1-butene content from 0 to 30 mol % were prepared by the gas-phase polymerization process with isospecific Ziegler−Natta catalysts. The propylene sequences of the copolymers obtained are essentially high isotactic without head-to-head or tail-to-tail monomeric units and are totally consistent with all copolymers with various 1-butene contents.

Carbon-13 NMR Measurement. Sample solutions were prepared for the carbon-13 NMR measurements by dissolving approximately 10 wt % the copolymer samples in *o*-dichlorobenzene-d_4 solvent. Because the chemical shifts change with factors such as experimental temperature and solvent, in this set of experiments the highest peak, at 132.99 ppm in *o*-dichlorobenzene-d_4, is defined as the standard reference, according to a polyethylene sample (30.00 ppm). Carbon-13 NMR spectra were recorded on a Bruker Avance DMX 400 MHz spectrometer operated at 100 MHz at 125 °C. The experimental conditions are summarized as follows: 10 mm o.d. glass tube; 90° pulse flip angle; 150 ppm sweep width; 2 s acquisition time; 15 s delay time; more than 10K scans. To eliminate the NOE, an inverse-gate decoupling pulse program was selected. In measurements of the carbon-13 NMR spectrum, the proton broadband noise decoupling program of Walth16 was used to remove $^{13}C-^{1}H$ coupling.

Result and Discussion

Although the aim of this study is to recommend a new method for quantitatively determining monomer sequence distributions by minimizing the effect of configurarional distributions of propylene sequence, it is necessary to first discuss the carbon-13 NMR chemical shift assignments in propylene−1-butene copolymers. Figure 1 shows the carbon-13 NMR spectrum of a selected propylene copolymer with 8.17 mol % 1-butene comonomer, most peaks of which can been identified and assigned in terms of the previous assignments.[1−9] However, a few peaks in the experiment remain unclear. It was natural to link these new peaks to the configurational structure of propylene sequence, since the samples used in the study contained small amounts of 1-butene, and from comparison of the chemical shifts of these peaks with those of a propylene homopolymer[11] it was concluded that such a link was reasonable. The main explanation of the peaks resulting from propylene sequences configuration is that the samples used in this experiment have comparatively longer propylene sequences. Experimental results clearly show that the peaks arising from configurational sequence distributions seriously intermingle with those of comonomeric sequence distributions, indicating that this 400 MHz high-field NMR can give not only a fine comonomeric sequence structure, such as sequences of hexads, but also some configurational sequence structures in propylene−1-butene copolymers, such as sequences longer than the heptad. Thus, this study shows that the effect of the propylene sequence configuration on the monomer sequence distributions cannot be ignored, and it is necessary to focus attention on those peaks arising from configurational distributions of propylene sequence, so that any error in quantitative determination of monomer sequence distributions can be significantly decreased. More detailed discussion of the carbon-13 NMR chemical shift assignments of this copolymer is considered in the next paragraphs, including the PP-centered methylene region, the P-centered methine and B-centered branch methylene region, and the P-centered methyl region. All chemical shift assignments in propylene−1-butene copolymers, both configurational se-

Table 1. Chemical Shift Assignments in Propylene−1-Butene Copolymers

peak no.	sequence	integrated region, ppm	shift, ppm	more detailed sequences	carbon
1	BPPB	47.85−47.14	47.20	BPPB	ααP
2	BPPP	47.14−46.79	47.05	PPPPPP (*mmmrm*)	ααP
			46.88	PPPB	ααP
3	PPPP	46.79−45.75	46.76	PPPPPP (*mmmmr*)	ααP
			46.62	PPPPPB	ααP
			46.59	PPPPPP (*mmmmm*)	ααP
			46.42	PPPPPP (*mmrrr*)	ααP
4	BPBP + BPBB	44.10−43.67	43.76	BPBP + BPBB	ααPB
5	PPBP + PPBB	43.67−43.11	43.47	PPBP + PPBB	ααPB
6	BB	40.62−40.15	40.38	BB	ααBB
7	B	35.62−35.03	35.41	PBP	B-CH
			35.34	PBB	B-CH
			35.17	BBB	B-CH
8	P	29.55−28.45	29.15	BPB	P-CH
			29.04	PPB	P-CH
			28.99	PPPPP (*mmmm*)	P-CH
			28.80	PPPPP (*mmmr*)	P−CH
			28.69	PPPPP (*mmrm*)	P-CH
			28.53	PPPPP (*mmrr*)	P-CH
9	PBP	28.46−28.23	28.37	PPBPP	b-CH_2
			28.34	PPBPB	b-CH_2
			28.31	BPBPB	b-CH_2
10	PBB	28.23−27.99	28.16	PPBBP	b-CH_2
			28.13	PPBBB	b-CH_2
			28.10	PBBPB	b-CH_2
			28.00	BPBBB	b-CH_2
11	BBB	28.00−27.43	27.91	PBBBP	b-CH_2
			27.84	PBBBB	b-CH_2
12	P	22.18−21.43	21.89	PPPPPPP (*mmmmmm*)	P-CH_3
			21.87	PPPPB	P-CH_3
			21.83	BPPPB	P-CH_3
			21.77	PPPBP	P-CH_3
			21.74	PPPBB + PBPPB	P-CH_3
			21.71	BPPBB + PPPPPPP (*rmmmmr*)	P-CH_3
			21.64	PBPBP + PPPPPPP (*mmmmrm*)	P-CH_3
			21.61	PBPBB	P-CH_3
			21.59	BBPBB	P-CH_3
			21.11	PPPPP (mmrm+rmrr)	P-CH_3
			20.37	PPPPP (*mrrr* + *rrrr*)	P-CH_3
			19.97	PPPPP (*mrrm*)	P-CH_3
13	B	11.36−10.18	11.11	PBP	B-CH_3
			11.04	PPB	B-CH_3

quence distributions and comonomeric sequence distributions, are summarized in Table 1.

Figure 2 shows the expanded PP-centered methylene region from 47.85 to 45.75 ppm in two reference systems: a propylene homopolymer and a propylene copolymer with 8.17 mol % 1-butene comonomer. According to the previous assignments,[1−9] there should only be peaks related to the comonomeric sequences of three tetrad BPPB, PPPB, and PPPP in this region. However, because of stereoregularity, the propylene sequence can be further split into a variety of sequences with various tacticity. These correspond to propylene sequences with various monomeric units, such as dyad sequences, tetrad sequences, and even longer *n*-ads, like hexad sequences.[11] In other words, because of configurational splitting, tetra sequence PPPP occupies a wider region than previously thought.[1−9] It is clear that serious overlap of the peaks between configurational sequence distributions and comonomeric sequence distributions broadens the peaks in this region and makes them more complex. Basically, in addition to the chemical shift assignments of the peaks corresponding to comonomeric sequence distributions,[1−9] the peaks related to configurational distributions of propylene sequences, based on Busico's paper, can be easily identified and assigned:[11] for example, the peak at 47.05 ppm for hexad sequence PPPPPP (*mmmrm*), 46.76 ppm for PPPPPP (*mmmmr*), 46.59 ppm for PPPPPP (*mmmmm*), and 46.42 ppm for PPPPPP (*mmmrr*). Moreover, experimental results and the previous assignments also indicate that the configurational sequence sensitivity of this copolymer is much higher than its comonomeric sequence sensitivity. For example, the configurational

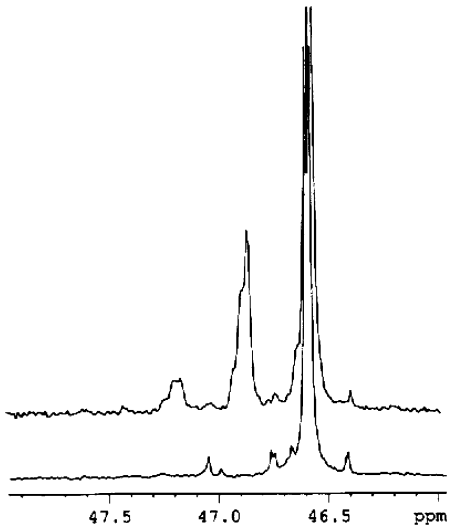

Figure 2. Expanded PP-centered methylene region in two reference systems: a propylene homopolymer (bottom) and a propylene copolymer with 8.17 mol % 1-butene (top) from 47.85 to 45.75 ppm.

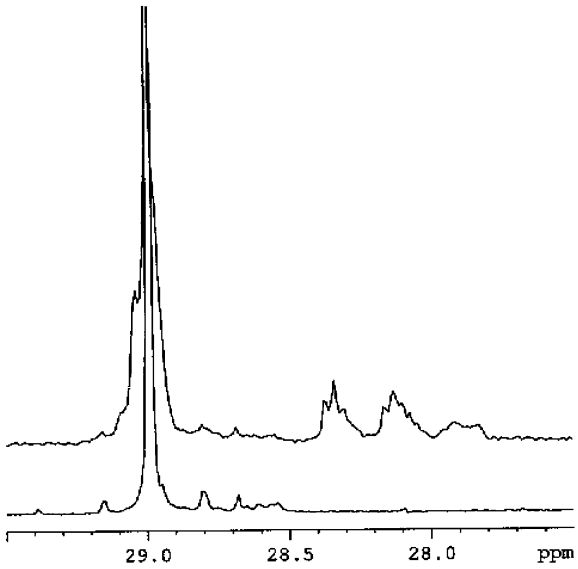

Figure 3. Expanded region of the P-centered methine and branch-methylene of 1-butene (2B) in two reference systems: a propylene homopolymer (bottom) and a propylene copolymer with 8.17 mol % 1-butene (top) from 29.55 to 27.43 ppm.

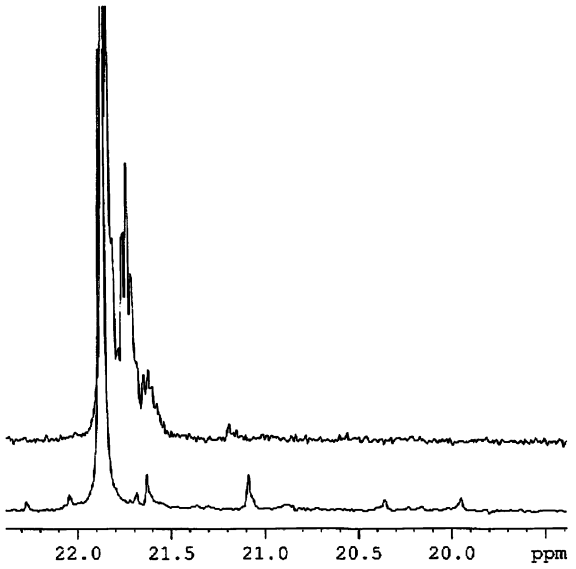

Figure 4. Expanded region of the P-CH_3 in two reference systems: a propylene homopolymer (bottom) and a propylene copolymer with 8.17 mol % 1-butene (top) from 22.18 to 21.43 ppm.

distribution of αα PP-centered tetrad sequences spreads in a wider range, of almost 2.10 ppm, from 45.75 to 47.85 ppm.[11] However, the corresponding tetrad comonomeric sequence distributions are only in a range of less than 0.50 ppm.[6−8] Concretely speaking, the split between the tetrad comonomeric sequences PPPB and PPPP is approximately 0.30 ppm, whereas the split between the tetrad configurational sequences PPPP (*mmr*) and PPPP (*mmm*) is almost 1.00 ppm,[11] that is, over three times that of the previous split. Therefore, this intermingling must result in greater difficulty both in assigning peaks and in the quantitative determination of monomer sequence distributions. To simplify the analysis, we define three regions based on the tetrad comonomeric sequences of the copolymers. For example, the region from 47.14 to 46.79 ppm, occupied by the tetrad comonomeric sequence PPPB, includes not only the tetrad comonomeric sequence PPPB but also some configurational sequences such as the PPPP (*mmr*) and PPPP (*rmr*). Similarly, the region from 47.85 to 47.14 ppm includes both the tetrad comonomeric sequences BPPB and at least part of the tetrad configurational sequences PPPP (*rmr*). For the same comonomeric and configurational reason, it can be determined that the region from 46.79 to 45.75 ppm represents only part of the tetrad sequence PPPP and not all of it. Thus, it is necessary to extract the quantities of the virgin peak area relating to the tetrad sequences PPPP, to determine the monomer sequence distributions in propylene−1-butene copolymers with the highest possible accuracy. Moreover, from Figure 2 we can assume that the lower the content of the 1-butene, the more serious the effect of configurational sequence distributions on comonomeric sequence distributions, thus the higher the error in quantitative determination of the area of corresponding peaks.

The region from 29.55 to 27.43 ppm, shown in Figure 3, is the most complicated and important part of the spectrum, and includes both the triad monomer sequence distributions of P-centered methine and the triad monomer sequence distributions of B-centered methylene in its branch. According to the previous assignment[1−9,11] and this expanded spectrum, it is clear that the methylene carbon in the branch of the 1-butene unit has higher monomer sequence sensitivity, (making the peaks relating to the B-centered triad comonomeric sequence distributions even longer *n*-ads sequence distributions), is comparatively isolated and is easily identified, and accurate content of B-centered triad sequences can be directly obtained from it. However, the triad comonomeric sequence sensitivity of P-centered methine is comparatively much lower, even though 400 MHz high-field NMR cannot resolve it well. Clearly, such serious peak overlaps make it impossible to gain accurate content of the P-centered triad monomer sequences directly from these peaks. By comparing this extended spectrum with that of Busico,[11] a few peaks on upfield are logically confirmed to be related to configurational distributions of propylene sequence: for example, peaks at 28.99 ppm for pentad PPPPP (*mmmm*), 28.80 ppm for PPPPP (*mmmr*), 28.69 ppm for PPPPP (*mmrm*), and 28.53 ppm for PPPPP (*mmrr*).

Figure 4 shows the extended carbon-13 NMR peaks of the methyl carbon in the propylene unit. According to the previous assignments[1−9,11] and this expanded experimental result, it can be seen that methyl carbons have lower comonomeric sequence sensitivity than configurational sequence sensitivity. For example, differences among the triad comonomeric sequence distributions, PPP, PPB, and BPB, are less than 0.15 ppm; however, differences among the triad configurational sequence distributions, PPP (*mm*), PPP (*mr*) and PPP (*rr*), are over 0.80 ppm, that is to say, all the comonomeric sequences are compressed only in the region of the triad configurational sequence PPP (*mm*). Undoubtedly, in such a small region, the intermingling and serious peak overlaps must result in greater difficulty, not only in the chemical shift assignments of relative peaks, but also in the quantitative determination of monomer sequence distributions. Clearly, it is impossible to gain accurate content of P-centered triad sequences based on these methyl peaks.[6] As in the above-mentioned regions, the upfield peaks found must be related to the configurational sequence distributions of the propylene unit in terms of Busico:[11] that is, peaks at 21.11 ppm for pentad PPPPP (*mmrm* + *rmrr*), 20.37

Table 2. Monomer Content, Dyad Sequence Distributions, and Number Average Sequence Lengths in Propylene−1-Butene Copolymers

		sample I	sample II
monomer content, mol %	P	91.83	74.77
	B	8.17	25.23
dyad sequences	PP	83.81	58.12
	PB	15.09	31.65
	BB	1.09	10.22
no. of av sequence lengths	n_P	12.10	4.67
	n_B	1.14	1.65

ppm for PPPPP (*mrrr* + *rrrr*), 19.97 ppm for PPPPP (*mrrm*).

Once the carbon-13 NMR chemical shift assignments are finalized, they can be utilized to quantitatively determine the content of monomers (monads), dyad sequences and triad sequences, as well as to measure the number-average sequence lengths for uninterrupted runs of both 1-butene and propylene units, which are generally thought to be enough to characterize this copolymer molecular microstructure. In general, with respect to the monomer content, it is easy to immediately determine its quantity from the area of peaks related respectively to the methane, or methyl of propylene, as well as the methine, branch methylene or methyl of 1-butene. For example, by use of the area of peak 7, peaks 9−11, or peak 13, the 1-butene monomer content can be immediately obtained; and integrating peak 8 or peak 12 will also directly give the propylene monomer content. The relative equations are given as follows:

$$[P] = [\text{peak 8}] = [\text{peak 12}] \quad (1)$$

$$[B] = [\text{peak 7}] = [\text{peak 9}] + [\text{peak 10}] + [\text{peak 11}] = [\text{peak 13}] \quad (2)$$

In principle, the monomer content should be obtained in the simplest and most direct way. The data from peak 8 and peak 7, respectively, are summarized in Table 2.

In the same way, quantitative dyad sequences, PP, PB, and BB, can be easily obtained from the corresponding peak area of αα methylene carbon in the regions of 47.85−45.75 ppm (peaks 1−3), 44.10−43.11 ppm (peaks 4 and 5), and 40.62−40.15 ppm (peak 6), respectively, and the relative equations are listed as follows:

$$[PP] = [BPPB] + [PPPB] + [PPPP] = [\text{peak 1}] + [\text{peak 2}] + [\text{peak 3}] \quad (3)$$

$$[PB] = [BPBB] + [BPBP] + [PPBB] + [PPBP] = [\text{peak 4}] + [\text{peak 5}] \quad (4)$$

$$[BB] = [\text{peak 6}] \quad (5)$$

All data concerning the dyad sequence distributions are summarized in Table 2.

As for the triad sequence distributions, two steps are followed to determine their quantities: first, in this study, 400 MHz high-field NMR allows the use of the previous method suggested by Randall and Cheng[3−6] to obtain the quantity of B-centered triad sequences, BBB, PBB, and PBP;that is to say, B-centered triad sequence distributions can be quantitatively determined from the branch methylene carbon of 1-butene unit (2B), based on the intensity of area of peaks 7−9. The equations are given as follows:

Table 3. Triad Sequence Distributions in Propylene−1-Butene Copolymers

	PPP	PPB	BPB	BBB	PBB	PBP
sample I	75.08	16.46	0.32	0.15	1.88	6.10
sample II	47.77	21.89	5.73	4.86	10.03	9.72

$$[PBP] = [\text{peak 9}] \quad (6)$$

$$[PBB] = [\text{peak 10}] \quad (7)$$

$$[BBB] = [\text{peak 11}] \quad (8)$$

Second, P-centered triad sequences, PPP, PPB, and BPB, are determined. As mentioned above, the area of peaks of the methyl carbon generally cannot be directly used to determine quantitatively P-centered triad sequence distributions, like B-centered triad sequence distributions, because they have longer spin−lattice times, T_1, and serious peak overlaps owing to their lower comonomeric sequence sensitivity. If P-centered triad sequence distributions were determined on the basis of peaks in the methyl regions, as in the previous study,[3,6] serious peak overlaps and longer spin−lattice delay times, T_1, would result in greater error in the calculation of content, and the virgin quantity of P-centered triad sequences and the extent of error would not be known. Thus, it is impossible to obtain a first-hand accurate content of all triad sequences from a carbon-13 NMR spectrum.

To obtain a comparatively accurate quantity of P-centered triad sequence distributions, we propose a new method. According to the previous studies in monomer sequence distributions of ethylene−1-butene copolymer and ethylene−1-heptene,[13−15] we know there is a set of necessary relationship equations for all monomer sequences, available indirectly by obtaining the content of some monomer sequences. To obtain the set of P-centered triad sequence distributions, some relationship equations between the triad sequences and the tetrad sequences are employed. Peaks 1−3 represent the PP-centered tetrad sequences, BPPB, PPPB and PPPP, respectively, and consequently, the quantitative determination of the triad sequences, PPP, PPB, and BPB, can be achieved through the following equations (eqs 9−11). The content of corresponding P-centered triad sequences is summarized in Table 3.

$$[PPP] = [PPPP] + {}^1/_2[PPPB] = [\text{peak 3}] + {}^1/_2[\text{peak 2}] \quad (9)$$

$$[PPB] = [PPPB] + 2[BPPB] = [\text{peak 2}] + 2[\text{peak 1}] \quad (10)$$

$$[BPB] = [P] - [PPP] - [PPB] = [\text{peak 8}] - 2[\text{peak 1}] - {}^3/_2[\text{peak 2}] - [\text{peak 3}] \quad (11)$$

As discussed above, another factor, configuration, seriously affects the accuracy of the PP-centered tetrad sequence distributions, particularly the copolymers with comparatively small amounts of 1-butene. As shown in Figure 2, the coexistence of configurational sequence distributions and comonomeric sequence distributions makes the peak overlaps too extensive to calculate PP-centered tetrad monomer sequences, BPPB, PPPB, and PPPP, accurately. To minimize the effect of the config-

Table 4. Ratio of Configurational Sequence Distributions of a Propylene Homopolymer in the Three Defined PP-Centered Methylene Regions Matching Those of Copolymers

	peak I	peak II	peak III
polypropylene	7	266	10 000

Table 5. Modified Triad Sequence Distributions in Propylene−1-Butene Copolymers

	PPP	PPB	BPB	BBB	PBB	PBP
sample I	76.15	14.51	1.20	0.15	1.88	6.10
sampleII	48.40	20.75	6.24	4.86	10.03	9.72

uration of propylene sequences on the tetrad monomer sequence distributions, we propose that all propylene copolymers with various amounts of 1-butene have similar tacticities in the propylene sequence. Thus, by comparing the quantity of the areas of the tetrad sequence PPPP of a selected propylene copolymer with 0 mol % 1-butene, spreading in the respective three defined regions, and matching those of the copolymers, BPPB (47.85−47.14 ppm), PPPB (47.14−46.79 ppm), and PPPP (46.79−45.75 ppm), we can obtain a ratio of the areas of PPPP of the selected propylene homopolymer in the three respective regions. This ratio can then be used to determine the sequences of the copolymers by excluding the effect of the propylene sequence configuration. The ratio of the areas in the three defined regions is obtained by use of a configuration using eqs 12−15, and its numerical value is summarized in Table 4. Here, [peak III], [peak II], and [peak I] represent the area quantity of tetrad sequence, PPPP, of the selected homopolymer in the three defined regions, respectively.

$$[\mathrm{PPPP}(3)]:[\mathrm{PPPP}(2)]:[\mathrm{PPPP}(1)] = [\text{peak III}]:[\text{peak II}]:[\text{peak I}] = \mathrm{A:B:C} \quad (12)$$

$$[\mathrm{PPPP}(3)] = [\text{peak III}] \quad (13)$$

$$[\mathrm{PPPP}(2)] = [\text{peak II}] = [\mathrm{PPPP}(3)]\mathrm{B/A} = [\text{peak III}]\mathrm{B/A} \quad (14)$$

$$[\mathrm{PPPP}(1)] = [\text{peak I}] = [\mathrm{PPPP}(3)]\mathrm{C/A} = [\text{peak III}]\mathrm{C/A} \quad (15)$$

From the above set of eqs 13−15, the ratio of peak area in the three defined regions can be obtained, and by minimizing the effect of configuration, the content of the tetrad sequences BPPB, PPPB, and PPPP of propylene copolymers with various amounts of 1-butene can be modified from the following equations (eqs 16−18):

$$[\mathrm{PPPP}] = [\mathrm{PPPP}(3)](\mathrm{A} + \mathrm{B} + \mathrm{C})/\mathrm{A} = [\text{peak 3}]\,(\mathrm{A} + \mathrm{B} + \mathrm{C})/\mathrm{A} = \quad (16)$$

$$[\mathrm{PPPB}] = [\text{peak 2}] - [\mathrm{PPPP}(3)]\mathrm{B/A} = [\text{peak 2}] - [\text{peak 3}]\mathrm{B/A} \quad (17)$$

$$[\mathrm{BPPB}] = [\text{peak 1}] - [\mathrm{PPPP}(3)]\mathrm{C/A} = [\text{peak 1}] - [\text{peak 3}]\mathrm{C/A} \quad (18)$$

Combining the above set of equations with eqs 9−11, the P-centered triad sequence distributions can be modified and are summarized in Table 5. The experimental results suggest that the higher the 1-butene content in copolymers, the lower the effect of configuration of the propylene sequence on the tetrad monomer sequence distributions.

Table 6. Quantitative Verification and Comparison of Triad Sequence PPB Content Obtained in Various Ways

		BPPB (peak 1)	PPPB (peak 2)	calcd PPB	PPB (peak 5)
sample I		389	1589	2367	1867
	modified	382	1323	2087	
sample II		973	3421	5367	5121
	modified	966	3155	5087	

Number-average sequence length is another important index to characterize the molecular microstructure of propylene−1-butene copolymers, which may generally be determined from dyad sequence distributions by use of the following equations:[12]

$$\bar{n}_{\mathrm{P}} = \frac{(\mathrm{PP}) + {}^1/_2(\mathrm{BP})}{{}^1/_2(\mathrm{BP})} \quad (19)$$

and

$$\bar{n}_{\mathrm{B}} = \frac{(\mathrm{BB}) + {}^1/_2(\mathrm{BP})}{{}^1/_2(\mathrm{BP})} \quad (20)$$

The data concerning the number-average sequence length of samples is also given in Table 2.

To check the viability of the new method, we verified some selected necessary relationship equations among monomer sequences by use of the virgin data and the data in Tables 2 and 5. For example, peak 5, consisting of tetrad sequences, PPBB and PPBP, can determine the content of triad sequence PPB according to the following relationship equation:

$$[\mathrm{PPB}] = [\mathrm{PPBB}] + [\mathrm{PPBP}] = [\text{peak 5}] \quad (21)$$

When the [PPB] from eq 21 is compared with that from eq 10, a series of obtained data proves the new method, as shown in Table 6. Taking into account experimental error, the calculation results show clear agreement between eq 21 and eq 10, suggesting that the new method is acceptable for analyzing monomer sequence distributions in propylene−1-butene copolymers.

Moreover, based on the monomer sequence relationship equations and the analysis mentioned above, in addition to being directly obtained from the pattern of carbon-13 NMR, the content of the 1-butene monomer can also be obtained in at least two other ways (for example, eq 2), that is to say, from dyad sequence distributions or triad sequence distributions by use of the following relationship equations:

$$[\mathrm{B}] = [\mathrm{BB}] + {}^1/_2[\mathrm{PB}] \quad (22)$$

$$[\mathrm{B}] = [\mathrm{PBB}] + [\mathrm{PBP}] + [\mathrm{BBB}] \quad (23)$$

The content of 1-butene monomer obtained from the above-mentioned equations (eqs 2, 22, 23) are shown in Table 7. The result indicates that marginal error is low, suggesting that the method is reliable for characterizing propylene−1-butene copolymers.

By such positive quantitative verification, we have not only confirmed that the new method is effective in analyzing monomer sequence distributions in propylene copolymers with small amounts of 1-butene, particularly the P-centered triad sequence distributions, but also established that there is a consistent pattern, which

Table 7. Quantitative Verification and Comparison of 1-Butene Content Obtained in Various Ways

	triads				dyads			
	PBP peak 9	PBB peak 10	BBB peak 11	calcd B	PB peak 4 + peak5	BB peak 6	calcd B	B peak 7
sample I	877	270	22	1196	2157	156	1234.5	1175
sample II	2383	2459	1191	6033	7839	2531	6450.5	6237

holds true for other propylene-linear-1-olefin copolymers in general. At the same time, the study shows that the lower the 1-butene content in copolymers, the higher the effect of configuration of propylene sequence on its accuracy. With respect to the longer *n*-ad sequences, like tetrad sequences, we will not continue to analyze the distribution results because such work is similar to the triad sequence.

Conclusions

From the above discussions, it is concluded that the 400 MHz high-field NMR can be used to find fine configurational and comonomeric sequence structures in propylene−1-butene copolymers, and that the effect of configuration distributions of propylene sequences on the accurate determination of monomer sequence distributions cannot be ignored, particularly in the propylene copolymer with small amounts of 1-butene. The new method has been developed to quantitatively determine monomer sequence distributions, in particular P-centered triad sequence distributions, through use of monomer sequence relationship equations, which reliably minimize the error in the determination of monomer sequence distributions. It is also found that the lower the 1-butene content in copolymers, the higher the effect of configuration of propylene sequence on accuracy.

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