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A ^{13}C NMR Determination of the Comonomer Sequence Distributions in Propylene–Butene-1 Copolymers

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ABSTRACT: The copolymer composition and dyad, triad, and tetrad sequence distributions have been determined from ^{13}C-NMR data for a series of predominantly isotactic propylene–butene-1 copolymers. The propylene concentrations ranged from 57 to 77 mol %. Number average sequence lengths were determined from the observed dyad distributions and compared to that calculated assuming Bernoullian statistical behavior. A good Bernoullian fit was obtained for both the number average sequence lengths and the associated dyad, triad, and tetrad comonomer distributions. A complete set of NMR schemical shift assignments is given and compared to those predicted with the Grant and Paul parameters and compositional trends observed among the copolymers. A four unit or tetrad sequence was the longest sequence detected by ^{13}C NMR at 25.2 MHz.

A detailed representation of copolymer molecular structure is available from ^{13}C NMR because unlike connecting comonomer sequences can be detected independently of like connecting sequences. Quite often, this structural information is not limited to just dyads but also includes triad, tetrad, and even pentad connecting sequences.[1–3] Thus, copolymer structure can be determined with considerable detail. The translation of ^{13}C-NMR data to meaningful quantitative terms, however, is not always readily accomplished. The observed spectral information is also related to factors other than the simple comonomer distribution. Configuration and mode of addition can seriously complicate analyses of ^{13}C copolymer spectra.[1] All factors must be considered if the information retrieved is to portray accurately the structure of the copolymer system.[1] Correspondingly, the analyses are less tedious and excellent reference information is provided if copolymers are available where configuration is constant and inversions in the mode of monomer additions have not occurred.[2]

The propylene–butene-1 copolymers examined in this study were prepared under polymerization conditions that led to essentially isotactic, head-to-tail comonomer sequences.[4] Thus, inversion in the mode of monomer addition and multiple configurational arrangements were not a consideration in the ^{13}C-NMR analysis. Any multiplicities in chemical shifts for a particular carbon type could be attributed to differences in the comonomer sequence arrangements and not to configurational differences. Recently, in a study of related propylene-butene-1 copolymers, which were prepared with Zeigler catalysts and were rich in butene-1, Fisch and Dannenburg[5] obtained assignments for isotactic butene-1–butene-1 and butene-1–propylene sequences. These assignments have been extended by the present study because the relative concentrations of the two different monomer units in the series of copolymers examined were more nearly the same. Resonances were observed in the ^{13}C spectra for triad and tetrad comonomeric sequences in addition to the isotactic propylene–propylene dyad not detected in the earlier study.

With a finite set of dyads, that is, propylene–propylene (PP), propylene–butene-1 (PB), and butene-1–butene-1 (BB), the number average sequence lengths for both butene-1 and propylene monomer units can be calculated. This determination of number average sequence length is independent of any possible statistical fit or behavior and, therefore, is a true structural characteristic of these propylene–butene-1 copolymers. It is shown in this study that the comonomer sequence arrangements do, however, closely conform to a Bernoullian statistical model.

Experimental Section

The *propylene–butene-1 copolymers* examined in this study were prepared by methods reported previously.[4] The copolymer sequences are essentially isotactic and head to tail. Thus, the only structural variations outside of molecular weight and comonomer ratio occur among the arrangements possible for the butene-1 and propylene units. The ^{13}C spectra obtained were totally consistent with predominantly isotactic, head-to-tail sequences because the observed copolymer chemical shifts corresponded to those given in Table I for predominantly isotactic polypropylene and polybutene-1. Nonstereoregular polypropylene[6] and polybutene-1 (as observed in this laboratory) show extensive splittings, which were not observed in these copolymer spectra, for both the side chain and backbone carbon resonances.

Carbon-13 NMR spectra were obtained at 25.2 MHz from a Varian XL-100-15 spectrometer system equipped with a 16K FT-100 pulsed NMR computer system and a disk accessory. Spin–lattice relaxation times were obtained at 123 °C and a sweep width of 2500 Hz for each *of the major lines in the* ^{13}C *copolymer spectra*. The methylene carbons, in each location, consistently gave T_1 values below 1 s. The methine carbon T_1's ranged from 0.8 to 1.2 s while the methyl carbon T_1's were approximately 2 s for the propylene units and 3.5 s for the

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Table I
Assignments for the Observed Chemical Shifts[a] in a 68/32 Propylene–Butene-1 Copolymer and Reference Homopolymers, Polypropylene and Polybutene-1, which are Predominantly Isotactic

Propylene–butene-1 copolymer			Polypropylene	Polybutene-1	Fisch and	
Line	Carbon	δ (Me_4Si), ppm	δ (Me_4Si), ppm	δ (Me_4Si), ppm	Dannenburg	Assignment
1	αα-CH_2	47.1				BPPB
2	αα-CH_2	46.8				PPPB
3	αα-CH_2	46.5	46.5			PPPP
4	αα-CH_2	43.6				BPBP + PPBB
5	αα-CH_2	43.3			43.1	PPBP + BPBB
6	αα-CH_2	40.3		40.1	39.6	BB
7	CH	35.2		34.9	34.4	B
8	CH	28.9	28.5		28.2	P
9	2-CH_2	28.2				PBP
10	2-CH_2	28.0				PBB
11	2-CH_2	27.8		27.7	27.5	BBB
12	CH_3	21.8	21.8			PPP
13	CH_3	21.7				PPB
14	CH_3	21.5			21.4	BPB
15	CH_3	11.0				PBP
16	CH_3	10.9				PBB
16s	CH_3	10.8		10.8	10.9	BBB

[a] Chemical shifts measured with respect to an internal hexamethyldisiloxane standard and converted to Me_4Si by adding 2.03 ppm.

Table II
Observed Relative Intensities for Butene-1–Propylene Copolymers, A through H, as Measured by Spectral Integration

	Resonance														%
	1[a]	2[a]	3[a]	4[a]	5[a]	6[a]	7[b]	8[b]	9[c]	10[c]	11[c]	12[d]	13[d]	14[d]	15 + 16	propylene[f]
δ, ppm	47.1	46.8	46.5	43.6	43.3	40.3	35.2	28.7	28.2	28.0	27.8	21.5	21.7	21.5	11.0 + 10.9	
A	0.08	0.20	0.31	0.12	0.23	0.06	0.24	0.76	0.12	0.08	0.03	0.47	0.25	0.05	0.23	77
B	0.09	0.17	0.29	0.13	0.24	0.08	0.27	0.73	0.13	0.10	0.03	0.38	0.26	0.10	0.26	74
C	0.09	0.17	0.25	0.14	0.24	0.11	0.31	0.69	0.13	0.12	0.05	0.36	0.29	0.06	0.29	70
D	0.08	0.17	0.25	0.15	0.23	0.12	0.32	0.68	0.14	0.13	0.04	0.36	0.24	0.09	0.31	69
E	0.10	0.17	0.22	0.17	0.24	0.11	0.34	0.66	0.16	0.10	0.06	0.37	0.23	0.08	0.31	68
F	0.05	0.17	0.24	0.16	0.26	0.12	0.32	0.68	0.15	0.12	0.04	0.32	0.28	0.11	0.29	69
G	0.09	0.15	0.19	0.17	0.25	0.14	0.37	0.63	0.15	0.13	0.08	0.32	0.26	0.08	0.34	64
H	0.08	0.13	0.11	0.25	0.23	0.21	0.41	0.59	0.14	0.17	0.12	← 0.57[e] →			0.43	57

[a] Resonance intensities 1–6 normalized to unity. [b] Resonance intensities 7 and 8 normalized to unity. [c] Resonance intensities 9–11 normalized to the average butene-1 concentration. [d] Resonance intensities 12–16 normalized to unity. [e] Resonances 12–14 are combined because of insufficient resolution. [f] Average of the percent of propylene calculated from the αα-methylene, methine, and methyl carbon resonances.

butene-1 units. Consequently, a pulse spacing of 11.0 s was considered adequate for the ^{13}C-NMR measurements. The specific spectrometer conditions for the pulsed NMR measurements are summarized below:

pulse width	53 μs (90° flip angle)
sweep width	5000 Hz
acquisition time	1.5 s
pulse delay	9.5 s
number of transients	8–10K

Absolute intensities were compared for the methyl carbon resonances, backbone methylene, and the methine carbon resonances. These intensities were found to be generally within 5%; thus, no differences were indicated among the nuclear Overhauser effects. Full nuclear Overhauser effects were indicated after comparing the total spectral intensity with and without spin decoupling for the same number of accumulated transients.

Copolymer sample solutions were prepared for the NMR measurements by dissolving the copolymer samples into 1,2,4-trichlorobenzene and adding sufficient perdeuteriobenzene to maintain a lock signal. The final solution concentrations were approximately 10 wt % copolymer. Spectra were than recorded at 123 °C and referenced to an internal hexamethyldisiloxane internal standard. The chemical shifts reported in Table I, however, were changed to a Me_4Si internal standard by adding 2.03 ppm.

A complete set of relative areas, as determined from the ^{13}C-NMR spectra of these copolymers, is given in Table II. These measurements were not determined from a single scan but were determined from a series of measurements after dividing the spectra into four separate regions: (a) the αα-methylene carbon region which includes resonances 1 through 6, (b) the methine carbon region which includes resonances 7 and 8, (c) the side-chain methylene carbon region, resonances 9–11, and (d) the methyl carbon region which includes resonances 12–16. The areas from regions (a), (b), and (d) were normalized to unity; however, the areas from (c) were normalized to the average butene-1 mole percent observed for the copolymer. By treating the measurements and subsequent data in this manner, one obtains measurements which were made with the best possible precision and results which can be readily used in compositional determinations and comparisons of spectral assignments.

Results and Discussion

A ^{13}C-NMR spectrum of a 68/32 propylene–butene-1 copolymer, which is typical of the copolymers examined, is shown in Figure 1. At least 16 lines, which are numbered consecutively from low to high field, are present as compared to 7 lines observed by Fisch and Dannenburg[5] in a study of related butene-1–propylene copolymers. More lines are observed in these ^{13}C copolymer spectra because of a higher

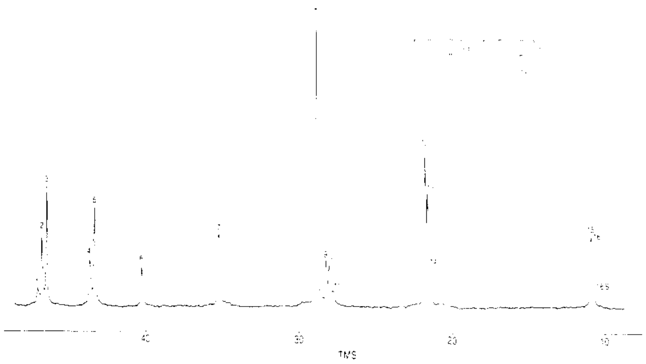

Figure 1.

propylene content which allows the propylene-centered triads and tetrads to be observed. Complete assignments are given in Table I. Seven assignments had been made previously by Fisch and Dannenburg and two more could be made through comparison with a spectrum of a predominantly isotactic polypropylene. These reference chemical shifts and those from a predominantly isotactic polybutene-1 are also included in Table I. The remaining new assignments were made by noting intensity changes with changes in the copolymer compositions and then confirmed by off-resonance decoupling and by comparison with calculated chemical shifts using the Grant and Paul parameters.[7,8]

The most valuable structural information, obtained from ^{13}C spectra, is found in the resonance pattern observed for the methylene carbons sandwiched between two methine carbons. These carbons, hereafter, will be referred to as $\alpha\alpha$-methylene carbons as suggested by Carman.[9] Six resonances for the $\alpha\alpha$-methylene carbons are present in the ^{13}C spectrum of Figure 1. Ten lines are anticipated if a complete tetrad sensitivity is observed while only three are expected for a dyad sensitivity. As it turns out, the observed spectrum for the $\alpha\alpha$-methylene carbons corresponds to a mixed dyad–tetrad chemical shift sensitivity with some overlap encountered among the tetrad resonances. The assignments, as listed in Table I, are BPPB, BPPP, PPPP, BPBP + BBPP, BBPB + PPBP, and BB from low to high field. A detailed discussion of these assignments is given in the following paragraphs.

The highest field $\alpha\alpha$-methylene carbon resonance at 40.3 ppm was assigned to the BB dyad by Fisch and Dannenburg after examination of copolymers which were 93–98% butene-1. No splitting or multiplicity of the 40.3 ppm resonance was observed over the range of copolymer compositions examined. A similar observation was made in the present study where the butene-1 concentration ranged from 23 to 43 mol %. Thus, it appears that the dyad chemical shift sensitivity proposed for the $\alpha\alpha$-methylene carbons in butene-1–butene-1 sequences is confirmed. The only other $\alpha\alpha$-methylene carbon assignment made by Fisch and Dannenburg was at 43.1 ppm for a BP dyad. This resonance also showed no multiplicities over the range of compositions examined; however, in this study, two resonances were present at 43.3 and 43.6 ppm. Upon inspection of the data presented by Fisch and Dannenburg, it appears likely that their 43.1-ppm resonance coincides with the 43.3-ppm resonance observed in this study and should be assigned, in part, to the BPBB tetrad. Since no PP dyad sequences were detected by Fisch and Dannenburg, only isolated P units were indicated and the BPBB assignment appears conclusive. The remaining PB-centered tetrads, BPBP, PPBB, and PPBP, are not likely to be present when the propylene concentration is only a few mole percent. With BPBB assigned, there are only four possibilities (Chart I) for the 43.3 and 43.6 ppm assignments.

The merits of each of these assignments can be judged by

Chart I

	43.6 ppm	43.3 ppm
(a)	PPBP + BPBP + PPBB	BPBB
(b)	PPBP + BPBP	PPBB + BPBB
(c)	PPBB + PPBP	BPBP + BPBB
(d)	BPBP + PPBB	PPBP + BPBB

noting the intensity changes with composition, given in Table II, and the necessary relationships for B,P sequences given below:[10]

$$\mathrm{PPBB + PPBP = PPPB + 2BPPB} \tag{1}$$

$$\mathrm{BPBP + PPBP = 2PBP} \tag{2}$$

$$\mathrm{PPBB + BPBB = BBP} \tag{3}$$

Assignment (a) can be safely eliminated from consideration because the 43.3-ppm resonance is consistently more intense than the 43.6-ppm resonance over a range of propylene concentrations from 64–77 mol %. The propylene-rich BP-centered tetrads should dominate over this range of propylene concentrations; thus, the 43.3- and 43.6-ppm resonances are composed of two overlapping tetrads in each case. Assignments (b) and (c) can be evaluated through the use of eq 1–3 above; however, before this can be accomplished, the PP-centered tetrad assignments for the $\alpha\alpha$-methylene carbons must be made along with the butene-1-centered triads which can be measured in the side-chain methylene region near 28 ppm.

The first three $\alpha\alpha$-methylene carbon resonances at 47.1, 46.8, and 46.5 ppm are assigned to the PP-centered tetrads, BPPB, PPPB, and PPPP, respectively. The assignment at 46.5 ppm could be made by comparison with the corresponding polypropylene resonance, which has also been shown to be tetrad sensitive.[11] The assignments for BPPB at 47.1 ppm and PPPB at 46.8 ppm follow because PPPB is expected to be more concentrated than BPPB over this range of propylene concentrations. A complete set of relative areas vs. copolymer composition is given in Table II.

Three side-chain methylene carbon resonances are observed at 28.2, 28.0, and 27.8 ppm and can be assigned in order to PBP, PBB, and BBB. The BBB triad resonance is assigned by comparison with the reference copolymer data of Fisch and Dannenburg and by comparison with the chemical shifts from a predominantly isotactic polybutene-1, given in Table I. The resonance at 28.2 ppm is assigned to PBP because this triad is expected to dominate the other two in these propylene-rich copolymers.

With the assignments completed for the B-centered triads and the PP-centered tetrads, the relative intensities can be used in eq 1–3 to test assignments (b) and (c) for the BP-centered tetrad resonances at 43.3 and 43.6 ppm. In the case of assignment (b), the relative intensities predicted for the 43.3- and 43.6-ppm resonances were opposite to that observed. For assignment (c), the calculated relative intensity for PPBB + BPBP is off by approximately a factor of 2. Thus, assignments (b) and (c) can be eliminated and assignment (d) is obtained by default. The $\alpha\alpha$-methylene carbon assignments presented in Table I are, therefore, based on internal consistencies within the data itself. Since it is possible that either an error in a preceding assignment or a misleading intensity could lead to a subsequent mistaken assignment, the assignments for the BP-centered tetrads should be considered tentative. The entire set of assignments given in Table I, however, can be arrived at independently, through Bernoullian calculations of the relative intensities. Therefore, as will be seen later, these assignments are not only self-consistent but strengthened by a Bernoullian fit as well.

The only assignments not discussed are for the side-chain methyl groups for the butene-1 and propylene units. Methyl

Table III
Observed Chemical Shifts in Propylene–Butene-1 Copolymers and Corresponding Chemical Shifts Calculated with the Grant and Paul Parameters

Line	Carbon	Sequence assignment	Obsd	Calcd
1	αα-CH_2	BPPB	47.1	45.53
2	αα-CH_2	PPPB	46.8	45.47
3	αα-CH_2	PPPP	46.5	45.41
4	αα-CH_2	BPBP + PPBB	43.6	42.59 42.59
5	αα-CH_2	PPBP + BPBB	43.3	42.53 42.65
6	αα-CH_2	BB	40.3	39.77 (BBBB), 39.65 (PBBP)[a]
7	CH	B	35.2	35.55 (BBB), 34.81 (PBP)[a]
8	CH	P	28.9	27.68 (PPP), 28.42 (BPB)[a]
9	2-CH_2	PBP	28.2	28.30
10	2-CH_2	PBB	28.0	28.36
11	2-CH_2	BBB	27.8	28.42
12	CH_3	PPP	21.8	20.74
13	CH_3	PPB	21.7	20.80
14	CH_3	BPB	21.5	20.86
15	CH_3	PBP	11.0	11.74
16	CH_3	PBB + BBB	10.8	11.74 11.74

[a] Only the extremes in the calculated chemical shifts are given.

Table IV
Propylene–Butene-1 Comonomer Distributions as Measured Independently from Methylene, Methine, and Methyl Resonances

	Mol % propylene			
	I[a]	II[b]	III[c]	Av
A	77	76	77	77
B	74	73	74	74
C	70	69	71	70
D	69	68	69	69
E	70	66	69	68
F	67	68	71	69
G	64	63	66	64
H	56	59	57	57

[a] From methylene relative intensities. [b] From methine relative intensities. [c] From methyl relative intensities.

Table V
Dyad Distributions and Number Average Sequence Lengths for Propylene–Butene-1 Copolymers A through H

	BB	BP	PP	$\bar{n}_P$	$\bar{n}_B$	% P
A	0.06	0.35	0.59	4.4	1.3	77
B	0.08	0.37	0.55	4.0	1.4	74
C	0.11	0.38	0.51	3.7	1.6	70
D	0.12	0.38	0.50	3.6	1.6	69
E	0.11	0.41	0.49	3.4	1.5	68
F	0.12	0.42	0.46	3.2	1.6	69
G	0.14	0.42	0.43	3.0	1.7	64
H	0.21	0.48	0.32	2.3	1.9	57

Calculated Dyad Distributions and Number Average Sequence Lengths Assuming Bernoullian Statistics

% P	BB	BP	PP	$\bar{n}_P$	$\bar{n}_B$
77	0.05	0.35	0.59	4.3	1.3
74	0.07	0.38	0.55	3.8	1.4
70	0.09	0.42	0.49	3.3	1.4
69	0.10	0.43	0.48	3.2	1.4
68	0.10	0.44	0.46	3.1	1.5
64	0.13	0.46	0.41	2.8	1.6
57	0.18	0.49	0.32	2.3	1.7

resonances at 21.8, 21.7, and 21.5 ppm are assigned respectively to PPP, PPB, and BPB. These assignments are confirmed because the resonances at 21.8 and 21.5 ppm can be assigned by comparison with the reference polymer and copolymer data given in Table I. The butene-1 methyl resonances at 11.0, 10.9, and 10.8 are assigned respectively to PBP, PBB, and BBB. The 10.8 resonance appeared only as a shoulder and could not be distinctively resolved. These assignments are consistent with the order assigned to the side-chain methylene carbon resonances near 28 ppm.

Before leaving the subject of assignments, it may be valuable to discuss some limitations of the Grant and Paul parameters when making chemical shift assignments in polymers. Calculated chemical shifts, obtained with Grant and Paul parameter values derived for polymers,[8] are given in Table III. The calculated chemical shifts are quite useful for distinguishing dyads or carbons from different monomer units. They are not as useful, however, for triad and tetrad chemical shift assignments within a given carbon type. The calculated chemical shifts for both the propylene and butene-1-centered triads occur in an opposite order to the assignments given in Table I. The PP-centered tetrad assignments are in the same order as predicted with the Grant and Paul parameters; however, the BP-centered tetrad assignments could not be predicted using the Grant and Paul approach. These calculated chemical shifts are based on an availability of a viable value for ε, the chemical shift contribution from carbons five bonds away. Although it is difficult to obtain values for ε which are not within experimental error of the measurements, it, nevertheless, is generally positive.[7,8] Thus, the observed order for the various triad and tetrad chemical shifts may not depend upon ε. Variations among those factors producing upfield chemical shifts appear responsible for these observed differences. Thus, calculated chemical shifts probably should not be used to distinguish subtle differences among either triads or tetrads in ^{13}C copolymer spectra unless one is certain of the parameter values used in the analysis. Other methods, such as those employed in this study, may prove more reliable when characterizing subtle spectral features.

After the ^{13}C spectral assignments have been made, information is available to determine the percent propylene vs. percent butene-1, to measure the number average sequence lengths for uninterrupted runs of both butene-1 and propylene units, and finally to test the observed comonomer distributions for conformity to Bernoullian or Markovian statistical behaviors. As pointed out by Fisch and Dannenburg,[5] the percent propylene and percent butene-1 can be measured from more than one spectral region. In this study, similar results were achieved whether one took a ratio of the methyl

Table VI
Observed and Calculated (Bernoullian) Comonomer Triad Distributions for Propylene–Butene-1 Copolymers A through H

Observed distributions

	PPP	PPB	BPB	PBP	BBP	BBB	% P
A	0.47	0.25	0.05	0.12	0.08	0.03	77
B	0.38	0.26	0.10	0.13	0.10	0.03	74
C	0.36	0.29	0.06	0.13	0.12	0.05	70
D	0.36	0.24	0.09	0.14	0.13	0.04	69
E	0.37	0.23	0.08	0.16	0.10	0.06	68
F	0.32	0.28	0.11	0.15	0.12	0.04	69
G	0.32	0.26	0.08	0.15	0.13	0.08	64
H		← 0.57 →		0.14	0.17	0.12	57

Calculated distributions

% P	PPP	PPB	BPB	PBP	BBP	BBB
77	0.46	0.27	0.04	0.14	0.08	0.01
74	0.41	0.28	0.05	0.14	0.10	0.02
70	0.34	0.29	0.06	0.15	0.13	0.03
69	0.33	0.30	0.07	0.15	0.13	0.03
68	0.31	0.30	0.07	0.15	0.14	0.03
64	0.26	0.29	0.08	0.15	0.17	0.05
57	0.19	0.28	0.11	0.14	0.21	0.08

carbon resonances, the methine carbon resonances, or the methylene carbon resonances utilizing the relationships

$$B = BB + \tfrac{1}{2}BP \tag{4}$$

$$P = PP + \tfrac{1}{2}BP \tag{5}$$

The percent propylene, obtained from each of the three measurements, and the final average are given in Table IV. In general, agreement among the three approaches was within 1–2%. The spectral data was also tested for any differences among nuclear Overhauser effects (NOE) and none was found. Full NOE's are present and the spectral data can be used quantitatively without being unduly concerned about the nuclear Overhauser effect.

Number average sequence lengths can be determined from the dyad distributions using the following relationships:[12]

$$\bar{n}_P = \frac{(PP) + \tfrac{1}{2}(BP)}{\tfrac{1}{2}(BP)} \tag{6}$$

and

$$\bar{n}_B = \frac{(BB) + \tfrac{1}{2}(BP)}{\tfrac{1}{2}(BP)} \tag{7}$$

The dyad distributions, as measured from the relative intensities of the $\alpha\alpha$-methylene carbon resonances and the number average sequence lengths, calculated from eq 6 and 7, are given in Table V.

The average propylene concentrations, as given in Table IV, can be used as Bernoullian conditional probabilities to calculate comonomer distributions and number average sequence length expected for copolymers exhibiting Bernoullian behavior. The results for the various dyad distributions and number average sequence lengths are included in Table V. The overall compositional trends for the dyad distributions and number average sequence lengths conform to the Bernoullian model, which suggests an ideally random distribution of the two monomers. The system can be more thoroughly tested for conformity to Bernoullian behavior by examining triad and tetrad distributions. For these particular copolymers, a triad distribution could not be accurately obtained because of peak overlap; nevertheless, triad distributions, as measured from the butene-1 side-chain methylene carbon resonances and the propylene methyl groups, are given in Table VI along with the corresponding Bernoullian triad distributions. In spite of the difficulties encountered in measuring the lowest triad concentrations, one finds that the overall compositional trends are consistent with that for a Bernoullian distribution. A tetrad distribution was also calculated and is presented in Table VII. Only a partial tetrad distribution could be obtained experimentally and, once again, peak overlap and the low relative concentration likely affected the accuracy of the BPPB determination. The overall trends, as shown by the data in Table VII, however, reflect Bernoullian characteristics. It should be noted that the calculated tetrad combinations, BBPP + PBPB and BBPB + PBPP, give the best agreement with the observed relative intensities for the 43.3- and 43.6-ppm resonances.

With the BP-centered tetrad assignments established, the necessary relationships, defined by eq 1 through 3, can be used to determine experimentally the four individual BP-centered tetrad concentrations. In so doing, the PBPP tetrad was observed to generally have the highest relative concentration and the BBPB tetrad the lowest concentration as expected for

Table VII
A Partial (Observed) Tetrad Distribution and Total Calculated Distribution for Propylene–Butene-1 Copolymer Samples A through H

Observed distributions

	BPPB	BPPP	PPPP	BBPP + PBPB	BBPB + PBPP	BBBB + BBBP + PBBP	% P
A	0.08	0.20	0.31	0.12	0.23	0.06	77
B	0.09	0.17	0.29	0.13	0.24	0.08	74
C	0.09	0.17	0.25	0.14	0.24	0.11	70
D	0.08	0.17	0.25	0.15	0.23	0.12	69
E	0.10	0.17	0.22	0.17	0.24	0.11	68
F	0.05	0.17	0.24	0.16	0.26	0.12	69
G	0.09	0.15	0.19	0.17	0.25	0.14	64
H	0.08	0.13	0.11	0.25	0.23	0.21	57

Calculated distributions

% P	BPPB	BPPP	PPPP	PBPB	BBPP	BBPB	PBPP	BBBB	BBBP	PBBP
77	0.03	0.21	0.35	0.06	0.06	0.02	0.21	0.00	0.02	0.03
74	0.04	0.21	0.30	0.07	0.07	0.03	0.21	0.00	0.03	0.04
70	0.04	0.21	0.24	0.09	0.09	0.04	0.21	0.01	0.04	0.04
69	0.05	0.20	0.23	0.09	0.09	0.04	0.20	0.01	0.04	0.05
68	0.05	0.20	0.21	0.09	0.09	0.04	0.20	0.01	0.04	0.05
64	0.05	0.19	0.17	0.11	0.11	0.06	0.19	0.02	0.06	0.05
57	0.06	0.16	0.11	0.12	0.12	0.09	0.16	0.03	0.09	0.06

these propylene-rich copolymers. It is interesting that the resonances from the PBPP and BBPB tetrads overlapped so perfectly. Separate resonances could not be resolved even for sample H, which contained 43% butene-1 and had the highest BBPB concentrations of the copolymers examined.

Conclusions

The structural characterization of these propylene–butene-1 copolymers using ^{13}C-NMR techniques is essentially complete. The copolymer composition, dyad distribution, or number average sequence lengths can be accurately measured. Chemical shift assignments, which are internally consistent, are presented for the entire ^{13}C copolymer spectrum. Only the BP-centered tetrad assignments, which are reasonable considering the information available, should be considered tentative. The comonomer distributions, observed for these copolymers, appear to be Bernoullian over the range of compositions examined.

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Hydroxamic Acid Polymers. Effect of Structure on the Selective Chelation of Iron in Water

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ABSTRACT: Vinyl polymers bearing side chains terminated in hydroxamic acid (HA) groups were prepared by the following method. The reaction between methacryloyl chloride and either glycine, β-alanine, or γ-aminobutyric acid gave the corresponding amides. The terminal carboxyl group was activated by condensation with *N*-hydroxysuccinimide in the presence of dicyclohexylcarbodiimide. Polymerization was effected by azobis(isobutyronitrile) at 60 °C. The polymer was treated with methylhydroxylamine hydrochloride and triethylamine to give the hydroxamic acid polymer. Depending upon which amino acid was used in the first step, the spacing between hydroxamic acid groups along the polymer chain was 9, 11, or 13 atoms, the polymers being designated P-9, P-11, or P-13. The polymers form colored complexes with iron(III), $\lambda_{\max}$ about 430 nm for a 3:1 HA–Fe ratio and about 470 nm for a 2:1 HA–Fe ratio. Mole ratio plots showed that stable 3:1 complexes formed. The stability constants for the iron polymer complexes were measured by competition experiments between iron(III), the polymer, and EDTA or DTPA. The averages of several determinations at various pH values were: 0.42×10^{29} (P-9); 4.86×10^{29} (P-11); and 2.24×10^{29} (P-13). These results show that the stereochemistry of the system (HA spacing) is an important factor in the stability of the complex. Competition between iron and aluminum for the polymers showed that P-11 was about 10 times more selective for iron than P-9 or P-13. The largest stability complex for aluminum was for P-13 (2.96×10^{27}). Evidence is also presented to show that the 3:1 HA–Fe complexes are converted to 2:1 complexes in the presence of excess iron.

Ion exchange resins bearing chelating functional groups have long been of interest for removing specific metals from water. By appropriate selection of functional groups, resins have been designed to complex a variety of transition, alkaline earth, and alkali metals.[1–8] Many of these resins bind several metal ions and thus are somewhat limited in their selectivity.

Hydroxamic acids form well-known colored complexes with iron(III). In the case of certain naturally occurring trihydroxamic acids, the siderochromes,[9–11] which include the ferrioxamines and the ferrichromes, the stabilities of the iron(III) complexes are exceptional.[12] The cause of this high stability can be attributed not only to the high coordinative power of the hydroxamic acid for iron(III) but also to the number and spacing of the coordinative groups. In the evolution of these iron scavengers in living organisms, the spacing of hydroxamic acids became adjusted so that the three hydroxamic acids of the siderochrome fit precisely the required octahedral coordination sphere of the iron.

Using the naturally occurring trihydroxamic acids as models, it appeared reasonable that hydroxamic acid polymers would have a high affinity and selectivity for iron if the attached hydroxamic acids could be arranged to fit the octahedron of the iron(III) complex. Although resins based on hydroxamic acids have been synthesized in the past, none have been constructed with the idea of providing a spacing distance favorable for complex formation.

Earlier we showed that in the case of vinyl polymers bearing side chain hydroxamic acid groups, the stability of the iron complex was affected by the atomic chain spacing between neighboring hydroxamic acids.[13] An 11-atom spacing was found to be far superior to a 3-atom spacing, presumably because the larger 11-atom spacing would allow neighboring hydroxamic acids to readily fit the octahedral iron complex, whereas the 3-atom spacing would not. Molecular models had indicated that an 11-atom spacing should be about optimum for formation of the octahedral iron complex.

In order to test this idea and to see to what extent small