2.8 ppm were assigned to the methoxy protons and methine and methylene protons of the MA unit, respectively. The methine and methylene protons of the MA unit of the copolymer were found to be much more subject to deshielding than those of the homopolymer of MA. Similar behavior was observed for protons of the donor monomer unit in many alternating copolymers containing $TCNQF_4$ or TCNQ.[1] The deshielding arises conceivably from a neighboring powerful electron-withdrawing dicyanomethylene group when the MA unit is sandwiched between the $TCNQF_4$ units in the copolymer. Additional absorption at 1.8 ppm was assigned reasonably to methyl protons of the isobutyronitrile group, the radical initiator AIBN fragment. When the product obtained is considered as an oligomer composed of six $TCNQF_4$–MA units with a radical initiator AIBN fragment at an end, the ratio of protons of the isobutyronitrile group to methine and methylene protons of the MA units is calculated as 1:3, consistent with the found area ratio of the peaks at 1.8 ppm to the ones at 2.8 ppm in Figure 10c. The elemental analysis data and molecular weight of the product obtained are also compatible with the proposed oligomer. It can be concluded, therefore, that the copolymer obtained is indeed alternating even though oligomeric.

Copolymerization of $TCNQF_4$ with AN (e = 1.2[15]), with a much higher positive e value, was attempted in acetonitrile with and without AIBN. Neither copolymer of $TCNQF_4$ with AN nor homopolymer of AN was obtained, and the starting materials were recovered.

St (e = –0.8), MMA (e = 0.4), and MA (e = 0.6) were found to be alternatingly copolymerizable with $TCNQF_4$. While St and MMA copolymerize with $TCNQF_4$ spontaneously and rapidly, MA, which has the lowest electron density among them, does not copolymerize spontaneously at an appreciable rate and it can copolymerize alternatingly when radical initiator was added. Finally, AN (e = 1.2), with less electron density, is no longer copolymerizable with $TCNQF_4$ in any fashion. These copolymerization behaviors with $TCNQF_4$ were found to be related intimately to the polar character of the comonomers. Moreover, it should be emphasized that MMA and MA, with positive e values, are alternatingly copolymerizable with $TCNQF_4$ as donor monomers. This alternating tendency between MMA or MA and $TCNQF_4$ cannot be explained in terms of polar effects in Alfrey–Price's Q–e scheme because all of them carry positive e values and repulsive forces would be expected instead of attractive ones. It is proposed, therefore, that the great difference in polar character between $TCNQF_4$ and alternatingly copolymerizable comonomers (in a relative sense rather than on an absolute scale) may be one of the primary factors for their alternating tendency as proposed previously in the study of the amphoteric behavior of TMCQ[5] in its alternating copolymerizations.

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Ethylene–1-Butene Copolymers. 1. Comonomer Sequence Distribution

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ABSTRACT: A carbon-13 NMR method is presented for a quantitative determination of the comonomer distribution, the triad and tetrad sequence distributions, average sequence lengths, and run numbers in ethylene–1-butene copolymers. A series of hydrogenated polybutadienes and a poly(1-butene) served as reference systems for establishing chemical shift assignments and for determining optimum conditions for a quantitative development. A dependence of relative spectral areas upon concentrations was noted at polymer sample weight percents of 30 and higher. The method presented should be free of errors associated with differences in spectral line widths, peak overlap, difficulties in detailed assignments, and complexities introduced through a configurational sensitivity.

Introduction

1-Butene and 1-hexene are frequently used in ethylene polymerizations to control polymer density. By varying the amount of comonomer incorporated, it is possible to produce copolymers with densities in a range of 0.90–0.94 g/cm^3, a result which has led to a line of commercial polyethylenes known as linear low-density polyethylenes (LLDPE). Superior film and processing properties coupled with recent manufacturing developments have created a renewed interest in this area.

Commercial ethylene–1-butene copolymers contain principally isolated ethyl branches; however, dependent

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upon the overall 1-butene incorporation, substantial quantities of 1,3-diethyl branches (dimers), 1,3,5-triethyl branches (trimers), or even larger blocks of ethyl branches may be present. It is the purpose of this study to review the carbon-13 NMR chemical shift assignments previously given for these copolymers and present a method for characterizing ethylene–1-butene copolymers in terms of the respective comonomer concentrations, the triad and tetrad sequence distributions, the average run lengths (or sequence lengths) of each monomer, and, finally, a "run number" or the number of comonomer runs per 100 monomer units.

Experimental Section

The carbon-13 NMR spectra were recorded on a Varian XL-200 NMR spectrometer at 50.31 MHz. Instrument conditions were as follows: pulse angle, 90°; pulse delay, 15 s; acquisition time, 1 s; spectral width, 8000 Hz; number of data points per spectrum, 16K; and double-precision arithmetic. Sample measurements were taken at 125.0 °C with broad-band decoupling.

Results from eight broadly different polymers are reported in this study, including a poly(1-butene) homopolymer with over 98% isotactic dyads. The remaining samples were hydrogenated polybutadienes with 1,2-butadiene contents of 16.3, 36.1, and 58.4 mol % and ethylene–1-butene copolymers with 1-butene contents ranging from 2.0 to 14.0 mol %.

Polymer solutions for the carbon-13 NMR measurements were prepared in 1,2,4-trichlorobenzene, with concentrations maintained at 10% by weight. Observed chemical shifts were referenced to an internal HMDS standard and corrected to Me_4Si by adding 2.03 ppm. The number of transients taken for each spectrum was around 6000. Intensity measurements were made from integrated areas. A study of concentration effects on spectral peak heights, line widths, and integrated peak areas was performed by examining the same sample at concentrations of 3.0, 5.0, 10.0, 20.0, 30.0, 40.0, and 50.0 polymer wt %. With a pulse delay of 15 s and solution concentrations 30% and higher, the relative areas showed a concentration dependence. Below 20%, this concentration dependence of peak area virtually disappeared. An accompanying strong line width dependence on sample concentration was also evident even at 20% by weight, but not at 10% and lower concentrations. At sample concentrations below 10%, substantial losses in signal to noise occurred; however no other ill effects were detected. Lower sample concentration did lead to improvements in the observed resolution; even so, extensive overlap among many resonances prevented peak heights from being reliable for use in the development of a quantitative method for the ethylene–1-butene system.

Results and Discussion

Ethylene–1-butene copolymers and the analogous hydrogenated polybutadienes have been the subjects of several previous studies (see ref 1 and references therein). These polymers are similar structurally because both consist of a polymer backbone with recurring methylene units interrupted by ethyl branches. Extensive carbon-13 NMR assignments have been given for the hydrogenated polybutadienes;[2-4] however, not all of the key resonances for the ethylene–1-butene copolymers have been assigned and some literature assignments may be open to question. Dechter and Mandelkern[1] have reported the occurrence of head-to-head 1-butene units in ethylene–1-butene copolymers as a result of resonances observed at 31.7–31.8 and 24.57 ppm, respectively. For the ethylene–1-butene copolymers examined in this study, there is no resonance observed in the vicinity of 31.7 ppm and we propose an alternative assignment for a resonance observed at 24.5 ppm.

Complete carbon-13 NMR spectral assignments are difficult to obtain for both the hydrogenated polybutadienes and the ethylene–1-butene copolymers. Considerable complexity is introduced from a chemical shift sensitivity to both the comonomer sequence arrangements and possible configurational arrangements for any given sequence. For example, there are 10 unique tetrads possible for a simple A,B copolymer system but these 10 tetrads can give rise to 20 different configurational sequences. Of course, neither the observed sequence sensitivity nor the configurational sensitivity is restricted to any particular sequence length but they vary according to carbon type and environment.[4] Previous literature assignments have been based on comparisons to chemical shifts calculated through additivity relationships and reference polymers.[1,5] We believe the latter to be the better approach and, by so doing, we have made as many assignments as we consider reasonable in this study.

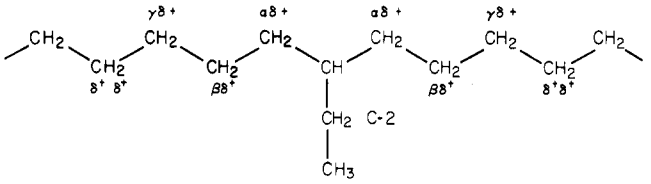
Predominantly isotactic poly(1-butene), the hydrogenated polybutadienes, and a series of ethylene–1-butene copolymers with known amounts of 1-butene incorporation are excellent model polymers for obtaining assignments for the ethylene–1-butene copolymer system. As shown in Table I, a poly(1-butene) containing predominantly isotactic sequences gives unequivocal assignments for the $\alpha\alpha$ methylene (BBBB, mmm), methine (BBB, mm), the branch methylene (BBB, mm), and the branch methyl (BBB, mm). (We will consistently utilize the nomenclature suggested by Carman[6] in a related study of ethylene–propylene copolymers where Greek letters were used to designate the proximity of each methine carbon relative to the backbone methylene carbon of interest. A methine carbon four or more removed was identified by δ^+.) An ethylene–1-butene copolymer containing only 2 mol % 1-butene has predominantly isolated ethyl branches and subsequently can lead to the unequivocal sequence assignments given in Table II. The hydrogenated polybutadienes were valuable as reference polymers because the 1,4- and the 1,2-butadiene additions preclude methylene sequences three carbons in length; thus the BEB moiety, in terms of ethylene and 1-butene units, is structurally impossible. The tetrad and triad E,B sequences shown in Table III, however, are possible (a 1,2 addition gives a B; a 1,4 addition gives an EE). The sequence assignments in Table III have been made previously for the hydrogenated polybutadienes and there is general agreement among independent studies.[2,3] Tetrads BEBE and BEBB and the associated triads BEB are missing structurally in hydrogenated polybutadienes; consequently a comparison of carbon-13 NMR spectra from a hydrogenated polybutadiene with that from an ethylene–1-butene copolymer can be useful in establishing the chemical shift locations of the $\alpha\gamma$ and $\beta\beta$ resonances from EBEB, BBEB, EBEBE, EBEBB, and BBEBB sequences, respectively. It should be noted in Figure 1, which contains spectra from an ethylene–1-butene copolymer and a hydrogenated polybutadiene where both possess similar amounts of ethyl branches, that the spectral regions near 24.5 and 34.5–34.8 ppm are considerably different. The resonances at 24.54 and 24.39 ppm are assigned to $\beta\beta$ carbons from the EBEBE and EBEBB sequences, respectively. A third resonance for BBEBB is anticipated for copolymers with a considerably higher block 1-butene content and is calculated to occur near 24.24 ppm. Resonances at 34.81 and 34.49 ppm are assigned, partially, to $\alpha\gamma$ for the sequences BEBB and EBEB, respectively. The intensities for the resonances from the $\alpha\gamma$ carbons should be twice that of the $\beta\beta$ carbons from the same structural sequence. That this is true is clear in the spectrum of the ethylene–1-butene copolymer in Figure 1 even though there is some resonance overlap between CH(BBB) and $\alpha\gamma$(BEBB) and also between $\alpha\gamma$(EBEB) and $\alpha\delta^+$(BBEE) (see Figure 2). The remaining assignments are given in

Table I
Chemical Shift Assignments and Spectral Regions for Quantitative Determinations for a Series of Hydrogenated Polybutadienes and Ethylene-1-Butene Copolymers

	hydrogenated polybutadienes			ethylene-1-butene copolymers				poly(1-butene) (isotactic)		
sequence	HB-1 16.3% "B"	HB-2 36.6% "B"	HB-3 58.4% "B"	EB-1 2.0% B	EB-2 6.3% B	EB-3 8.8% B	EB-4 14.0% B	100% B	region	peak
$\alpha\alpha$(BBBB)	40.0-39.8[a]	40.3-40.0[a]	41.2-39.7[a]			40.4-39.9[a]	41.0-39.8[a]	40.20	A	1-4
CH(EBE)	39.61[b]	39.62[b]	39.64[b]	39.65	39.61[b]	39.61[b]	39.61[b]			5
$\alpha\alpha$(BBBE)	39.56[a]		39.57[a]							6
$\alpha\alpha$(EBBE) (r)	39.28		39.31		39.30	39.29	39.28			7
$\alpha\alpha$(EBBE) (m)	38.97	38.97	38.99		38.97	38.98	38.98			8
CH(EBB)	37.23	37.23	37.24		37.23	37.24	37.24			9
CH(BBB)		35.1-34.8[a]	35.0-34.8[a]		35.0-34.8[a]	35.1-34.8[a]	35.1-34.8[a]	34.98	B	10-13
$\alpha\gamma$(BBEB)					34.80[c]	34.83[c]	34.81[c]			14
$\alpha\gamma$(EBEB)	(34.45)[d]	(34.46)[d]	(34.49)[d]	34.52	34.48[e]	34.48[e]	34.49[e]			15
$\alpha\delta^+$(BBEE)	34.36, 34.32	34.37, 34.32	34.34, 34.28		34.32	34.33	34.33			16
$\alpha\delta^+$(EBEE)	34.00	34.01	34.04	34.04	34.04	34.00	34.01			17
3 s				32.16	32.17	32.17				
$\gamma\gamma$(BEEB)	30.92	30.93	30.99		30.93	30.93	30.92		C	18
$\gamma\delta^+$(BEEE)	30.47	30.47	30.51	30.46	30.47	30.46	30.47			19
$\delta^+\delta^+$($(EEE)_n$)	29.99	29.99	30.01	29.98	29.98	29.98	29.98			20
C-2(BBB)	27.6-27.5[a]	27.6-27.4[a]	27.7-27.4[a]		27.7-27.4[a]	27.5	27.7-27.5[a]	27.70	D	21-23
$\beta\delta^+$(EBEE)	27.27	27.27	27.29	27.29	27.27	27.27	27.27			24
C-2(EBB) + $\beta\delta^+$(BBEE)	27.1-26.8[a]	27.1-26.9[a]	27.1-26.7[a]		27.1-26.8[a]	27.1-26.9[a]	27.1-26.8[a]			25-28
C-2(EBE)	26.67	26.66	26.66	26.71	26.67	26.68	26.68			29
$\beta\beta$(EBEBE)				24.54	24.54	24.54	24.54			30
$\beta\beta$(EBEBB)					24.38	24.36	24.39			31
$\beta\beta$(BBEBB)							(24.24)[f]			32
2 s				22.86	22.86					
1 s				14.07	14.08	14.06				
CH_3(EBE)	11.18	11.17	11.18	11.19	11.18	11.18	11.18		E	33
CH_3(EBB)	10.98[a]	10.98[a]	10.98[a]		11.02[a]	11.01[a]	11.02[a]			34
CH_3(BBB)	10.8-10.7[a]	10.9-10.6[a]	10.9-10.6[a]		10.86[a]	10.79[a]	10.9-10.7[a]	10.81		(35)

[a] Shows configurational "splitting". [b] Overlaps with one of the configurational splittings of $\alpha\alpha$(BBBE). [c] Overlaps with one of the configurational splittings of CH(BBB). [d] Not $\alpha\gamma$ but associated with $\alpha\delta^+$(BBEE). [e] Overlap of $\alpha\gamma$(EBEB) and one of $\alpha\delta^+$(BBEE). [f] Calculated.

Table II



branch carbons	backbone sequences	backbone carbons	backbone sequences
methine	EBE	$\alpha\delta^+$	EBEE
C-2	EBE	$\beta\delta^+$	EBEE
methyl	EBE	$\gamma\delta^+$	BEEE
		$\delta^+\delta^+$	$(EEE)_n$

Table III

polybutadiene sequence	corresponding E,B sequences and carbons: carbon	tetrad	triad
(1,2)-(1,4)-(1,2)	$\gamma\gamma$	BEEB	
(1,4)-(1,2)-(1,4)	methine, C-2, methyl		(E)EBE(E)
(1,4)-(1,2)-(1,4)	$\alpha\delta^+,\beta\delta^+$	EBEE	
(1,4)-(1,2)-(1,2)	methine, C-2, methyl		(E)EBB
(1,4)-(1,2)-(1,2)	$\alpha\delta^+,\beta\delta^+$	EEBB	
(1,4)-(1,4)	$\delta^+\delta^+$		$(EEE)_n$
(1,2)-(1,2)-(1,2)-(1,2)	methine, C-2, methyl		BBB
(1,2)-(1,2)-(1,2)-(1,2)	$\alpha\alpha$	BBBB	
(1,2)-(1,4)-(1,4)	$\gamma\delta^+$	BEEE(E)	
(1,4)-(1,2)-(1,2)-(1,4)	$\alpha\alpha$	(E)EBBE(E)	
(1,4)-(1,2)-(1,2)-(1,2)	$\alpha\alpha$	(E)EBBB	

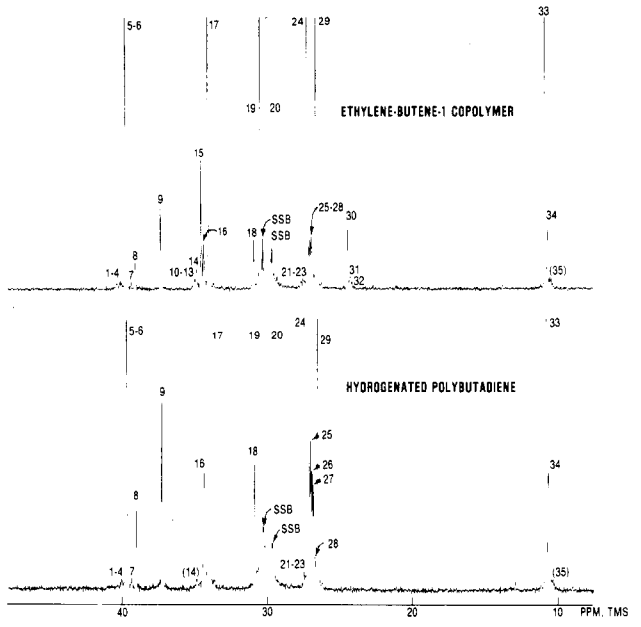


Figure 1. Carbon-13 NMR spectra at 50.3 MHz of EB-4 (14.0% 1-butene) (top) and HB-1 (16.3% 1-butene) (bottom) at 125 °C in 1,2,4-trichlorobenzene.

Table I. Dechter and Mandelkern assigned resonances at 24.57 and 31.73 ppm to the α resonance and the C-2 resonance of the head-to-head 1-butene units, respectively.[1] The 31.73-ppm resonance was missing in all the spectra that we have examined in this study. The nearest resonance to 31.73 ppm was the $\gamma\gamma$ resonance at 30.93 ppm for BEEB sequences. The resonance that we observed at

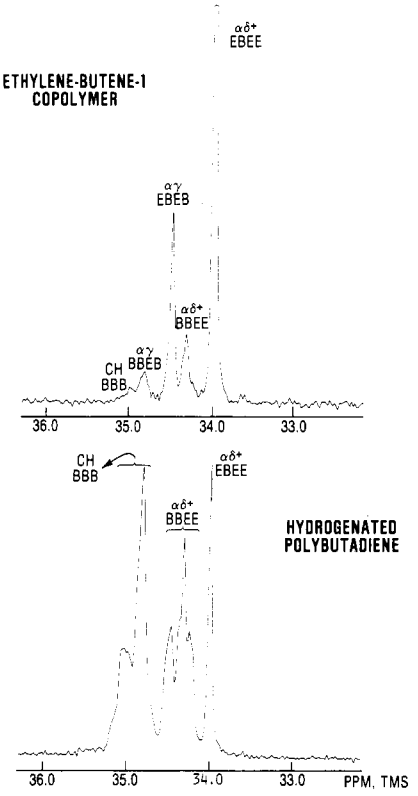


Figure 2. Region B depicting $\alpha\gamma$, $\alpha\delta^+$, and CH(BBB) resonances and possible configurational overlap for EB-4 (top) and HB-3 (bottom).

24.54 ppm unquestionably belongs to $\beta\beta$ for the EBEBE sequence.

There is an acute sensitivity to structural sequences manifested in the spectra of the ethylene–1-butene copolymers and the hydrogenated polybutadienes. Configurational chemical shifts complicate the sequence chemical shifts as is clearly evident in the cases of $\alpha\alpha$(BBBB), CH(BBB), C-2(BBB), C-2(BBE), CH_3(BBB), and CH_3(BBE). This is also true for the $\alpha\alpha$(BBBE) and $\alpha\delta^+$(BBEE) resonances. Unless one can be assured of having copolymer which is 100% isotactic, the assignments for sequences independently of configurational chemical shifts can never be certain. The inability to make specific configurational assignments as well as the observation that extensive overlap exists between resonances of known sequences, however, does not preclude an appropriate quantitative treatment of comonomer sequence distributions. For this particular copolymer system, it is possible to treat a group of not-so-well-resolved resonances of different carbon types collectively and mathematically deduce a complete and accurate triad distribution. Such an approach is discussed in the following paragraphs.

The carbon-13 NMR spectrum of an ethylene–1-butene copolymer is divided into regions labeled A–E as shown in Table I. Almost every region contains configurational "splitting", or broadening and shoulders from overlapping resonances from carbons of different types. Under this circumstance, a quantitative treatment based on single, specific identifications leading to a complete set of triads or tetrads would become tenuous and subject to considerable error. However, the triad information can be extracted from collective assignments with the help of the following relationships:

Let the average number of 1-butene runs of lengths 1, 2, 3, ..., x be designated by n_1, n_2, n_3, ..., n_x, respectively. The total number of 1-butene runs, N, per average molecule is therefore given by

$$N = n_1 + n_2 + n_3 + ... + n_x = \sum_{i=1}^{x} n_i \quad (1)$$

The total average number of 1-butene units, B, is likewise given by

$$B = n_1 + 2n_2 + 3n_3 + ... + xn_x = \sum_{i=1}^{x} in_i \quad (2)$$

Spectral region A is defined to include resonances for $\alpha\alpha$(BBBB), $\alpha\alpha$(BBBE), $\alpha\alpha$(EBBE), CH(EBE), and CH(BBE). The total intensity for this region, T_A, can be written in several ways as

$$T_A = \alpha\alpha(\text{BBBB}) + \alpha\alpha(\text{BBBE}) + \alpha\alpha(\text{EBBE}) + \text{CH(EBE)} + \text{CH(BBE)} \quad (3a)$$

$$= k([\text{B}] + N - n_1) \quad (3b)$$

$$= k([\text{BBB}] + \tfrac{3}{2}[\text{BBE}] + [\text{EBE}]) \quad (3c)$$

where k is the NMR constant, which can be removed later through normalization, and brackets indicate sequence mole fractions. Equation 3 is derived through the use of the following relationships:

$$\alpha\alpha(\text{BBBB}) = k[\text{BBBB}] = k(n_4 + 2n_5 + 3n_6 + 4n_7 + ... + (x-3)n_x) = k\sum_{i=4}^{x}(i-3)n_i \quad (4)$$

$$\alpha\alpha(\text{BBBE}) = k[\text{BBBE}] = 2k(n_3 + n_4 + n_5 + ... + n_x) = 2k\sum_{i=3}^{x} n_i \quad (5)$$

$$\alpha\alpha(\text{EBBE}) = k[\text{EBBE}] = kn_2 \quad (6)$$

$$\text{CH(EBE)} = k[\text{EBE}] = kn_1 \quad (7)$$

and

$$\text{CH(BBE)} = k[\text{BBE}] = 2k(N - n_1) \quad (8)$$

Similarly, the total intensity for region B can be written as

$$T_B = \text{CH(BBB)} + \alpha\gamma(\text{BBEB}) + \alpha\gamma(\text{EBEB}) + \alpha\delta^+(\text{BBEE}) + \alpha\delta^+(\text{EBEE}) \quad (9a)$$

$$= k([\text{B}] + n_1) \quad (9b)$$

$$= k([\text{BBB}] + [\text{BBE}] + 2[\text{EBE}]) \quad (9c)$$

$$= k([\text{BBB}] + [\text{BEE}] + 2[\text{BEB}]) \quad (9d)$$

because of the following relationships:

$$\text{CH(BBB)} = k[\text{BBB}] = k(n_3 + 2n_4 + 3n_5 + ... + (x-2)n_x) = k\sum_{i=3}^{x}(i-2)n_i \quad (10)$$

$$\alpha\gamma(\text{BBEB}) + \alpha\gamma(\text{EBEB}) + \alpha\delta^+(\text{BBEE}) + \alpha\delta^+(\text{EBEE}) = k[\text{BE}] = 2kN \quad (11)$$

and[7]

$$[\text{BBE}] + 2[\text{EBE}] = [\text{BEE}] + 2[\text{BEB}] \quad (12)$$

In region C, three peaks are grouped together

$$T_C = \gamma\gamma(\text{BEEB}) + \gamma\delta^+(\text{BEEE}) + \delta^+\delta^+ \quad (13a)$$

$$= 2k[\text{EEE}] + \tfrac{1}{2}k[\text{BEE}] \quad (13b)$$

where

$$\gamma\gamma(\text{BEEB}) = k[\text{BEEB}] \quad (14)$$

$$\gamma\delta^+(\text{BEEE}) = k[\text{BEEE}] \quad (15)$$

and

$$\tfrac{1}{2}\delta^+\delta^+ + \tfrac{1}{4}\gamma\delta^+ = k[\text{EEE}] \quad (16)$$

Region D is defined to include all the $\beta\delta^+$(BEE), $\beta\beta$(BEB), and C-2 resonances. For these resonances, we have

$$\text{C-2(BBB)} + \text{C-2(BBE)} + \text{C-2(EBE)} = k([\text{BBB}] + [\text{BBE}] + [\text{EBE}]) = k[\text{B}] \quad (17)$$

$$\beta\delta^+(\text{EBEE}) + \beta\delta^+(\text{BBEE}) = k([\text{EBEE}] + [\text{BBEE}]) = k[\text{BEE}] \quad (18)$$

and

$$\beta\beta(\text{EBEBE}) + \beta\beta(\text{BBEBE}) + \beta\beta(\text{BBEBB}) = k[\text{BEB}] \quad (19)$$

The total intensity of this region is, therefore,

$$T_D = k([\text{B}] + [\text{BEE}] + [\text{BEB}]) \quad (20a)$$

$$= k([\text{B}] + 2N - [\text{BEB}]) \quad (20b)$$

$$= k([\text{BBB}] + 2[\text{BBE}] + 3[\text{EBE}] - [\text{BEB}]) \quad (20c)$$

Region E contains only the branch methyl resonances. The total intensity of this region is thus simply

$$T_E = k[\text{B}] \quad (21)$$

Among the above-listed relationships, only six are needed for obtaining the complete triad distribution, providing that they all represent independent relationships.

In practice, each of the above-listed equations does not have equal applicability. To be more specific, eq 4, 5, and 7 cannot be used separately because of extensive overlap between resonances for $\alpha\alpha$(BBBE) and CH(EBE) and because of uncertainties in the configurational assignments and boundaries for the widely spread $\alpha\alpha$(BBBB) resonances. Equations 10 and 11 can also be classified into this category as a result of overlap between the CH(BBB) and $\alpha\gamma$(BBEB) resonances and also between the $\alpha\gamma$-(EBEB) and $\alpha\delta^+$(BBEE) resonances. In region C, the far-reaching "foothill" effect of the large $\delta^+\delta^+$ peak makes a separate quantitative intensity measurement of $\gamma\delta^+$-(BEEE) and $\delta^+\delta^+$ vulnerable to large errors. Extensive overlap between $\beta\delta^+$(EBEE), $\beta\delta^+$(BBEE), and the C-2 resonances makes an independent use of eq 17 and 18 almost impossible. Finally, the methyl region will give a low intensity for k[B] relative to that determined from the remainder of the spectral resonances because 15 s is an inadequate pulse delay.[8] As a result, eq (21) becomes inappropriate for use in the final quantitative treatment. In the interest of efficiency, the methyl resonances can safely be sacrificed as the remainder of the spectral resonances are satisfied by the 15-s pulse delay plus the 1-s acquisition time.

The key factor considered in the discussion above is the degree of accuracy possible when associating a single resonance intensity to a known specific comonomer sequence vs. a collective measurement of a group of comonomer resonances. For a triad sequence distribution analysis, we have found a total of six "reliable" associations for the ethylene–1-butene copolymer system. These are eq 3, 8, 9, 13, 19, and 20. Four of these are "collective" assignments for spectral regions A–D, while the other two are single, well-defined resonances from easily assignable sequences. Note that several alternative expressions are given to the four total intensities of the "collective" as-

signments. These expressions are derived through the use of the following three necessary relationships among sequence mole fractions[7]

$$[B] = [BBB] + [BBE] + [BBE] \quad (22)$$

$$[BEE] = [BEEE] + 2[BEEB] \quad (23)$$

and eq 12. In essence, the relationships we now have available are more than what is deemed necessary for solving for the six triad sequence mole fractions. Consequently, different quantitative treatments can be formulated depending upon the various combinations of discriminating choices. In the following paragraphs, we will discuss two such treatments.

Method A. General Approach. In the general treatment, we selected eq 3b, 9b, 19, 13b, 20a, and 20b. Equations 19 and 20b were combined to give

$$T_D + \beta\beta(BEB) = k([B] + 2N) \quad (24)$$

These equations are sufficient to solve for [B], N, and n_1; that is

$$k[B] = \tfrac{1}{3}(2T_A + 2T_B - T_D - \beta\beta(BEB)) \quad (25)$$

$$kN = \tfrac{1}{3}(2T_D + 2\beta\beta(BEB) - T_A - T_B) \quad (26)$$

$$kn_1 = \tfrac{1}{3}(T_B + T_D + \beta\beta(BEB) - 2T_A) = k[EBE] \quad (27)$$

In addition to eq 27 for k[EBE] and eq 19 for k[BEB], the unique triads are defined by

$$k[BBE] = \tfrac{2}{3}(T_D + \beta\beta(BEB) + T_A - 2T_B) \quad (28)$$

$$k[BBB] = \tfrac{1}{3}(2T_A + 5T_B - 4T_D - 4\beta\beta(BEB)) \quad (29)$$

$$k[BEE] = \tfrac{2}{3}(2T_D - T_A - T_B - \beta\beta(BEB)) \quad (30)$$

and finally

$$k[EEE] = \tfrac{1}{6}(3T_C + T_A + T_B + \beta\beta(BEB) - 2T_D) \quad (31)$$

The advantage of eq 19 and 27–31 in obtaining a complete triad distribution is that the integrated total intensities of the four spectral regions A–D are utilized to the fullest extent. One can have a relatively poorly resolved spectrum and still be able to do an adequate quantitative treatment. However, one final problem merits further discussion. Quite often, difficulties were experienced in obtaining reliable intensities for regions B and D because of spectral phasing problems associated with the "foothill" effects from the $\delta^+\delta^+$ resonance. As a result, we either overestimate T_B and underestimate T_D or vice versa. The opposite errors in T_B and T_D tend to cancel each other for [EBE] as was the case in eq 27. For the other triad sequences, this kind of error can be magnified. On the other hand, good phasing techniques can eliminate this source of error and, by so doing, make this particular approach the most desirable.

Method B. Method of Averaging. In a second method, we use eq 8 to replace T_B in one triad determination and to replace T_D in another. This approach leads to two sets of triad distribution values which are heavily dependent on T_B in one case and T_D in the other. Comparison of the two sets of values should give clear indications on the adequacy of spectral phasing. An average of the two sets should lead to a result which minimizes phasing errors. Both sets of equations are given below.

Equations 3c, 8, 9c, 9d, 13b, and 19 are used in the elimination of T_D. (The concentrations for [BBE] and [BEB] are given directly by eq 8 and 19, respectively.)

$$k[EBE] = T_B - T_A + \tfrac{1}{2}CH(BBE) \quad (32)$$

$$k[BBB] = 2T_A - 2CH(BBE) - T_B \quad (33)$$

$$k[BEE] = 2(T_B + CH(BBE) - T_A - \beta\beta(BEB)) \quad (34)$$

$$k[EEE] = \tfrac{1}{2}(T_C + T_A + \beta\beta(BEB) - T_B - CH(BBE)) \quad (35)$$

For the elimination of T_B, eq 9c and 9d are replaced by equations 20a and 20c. (This change dose not effect the equations for [BBE] and [BEB].)

$$k[EBE] = \tfrac{1}{4}(2T_D + 2\beta\beta(BEB) - 2T_A - CH(BBE)) \quad (36)$$

$$k[BBB] = \tfrac{1}{4}(6T_A - 5CH(BBE) - 2\beta\beta(BEB) - 2T_D) \quad (37)$$

$$k[BEE] = \tfrac{1}{2}(2T_D + CH(BBE) - 2T_A - 2\beta\beta(BEB)) \quad (38)$$

and

$$k[EEE] = \tfrac{1}{8}(4T_C + 2T_A + 2\beta\beta(BEB) - 2T_D - CH(BBE)) \quad (39)$$

For a direct determination of the final average, we have

$$k[EBE] = \tfrac{1}{16}(4T_B + 2T_D + 2\beta\beta(BEB) + CH(BBE) - 6T_A) \quad (40)$$

$$k[BBB] = \tfrac{1}{8}(14T_A - 13CH(BBE) - 2\beta\beta(BEB) - 4T_B - 2T_D) \quad (41)$$

$$k[BEE] = \tfrac{1}{8}(4T_B + 2T_D + 5CH(BBE) - 6T_A - 6\beta\beta(BEB)) \quad (42)$$

and

$$k[EEE] = \tfrac{1}{16}(8T_C + 6T_A + 6\beta\beta(BEB) - 5CH(BBE) - 4T_B - 2T_D) \quad (43)$$

Notice that in eq 40–43, T_B and T_D always have the same sign, which would ensure the canceling effect anticipated from this averaging process.

The validity of methods A and B has been tested with three hydrogenated polybutadienes where the concentration of BEB has to be zero. As shown in Table IV, test results confirm the validity of utilizing eq 8. With good spectral phasing, results from both methods agree very well. Furthermore, the absence of the BEB structural sequence in the hydrogenated polybutadienes leads to better separations among the CH(BBB), $\alpha\delta^+$(BBEE), and $\alpha\delta^+$(EBEE) resonances in region B, which are sufficient to allow direct measurements of [BBB], [BBE], and [EBE], respectively. Comparisons within the various data sets (Table IV) not only confirm, once more, the applicability of both methods A and B but also provide quantitative supplementary information about the existence of suspected overlap between CH(BBB) and $\alpha\gamma$(BBEB) resonances near 34.8 ppm and between the $\alpha\gamma$(EBEB) and $\alpha\delta^+$(BBEE) resonances near 34.5 ppm. Similar investigations show a trend toward lower T_E's when compared to k[B] with increasing 1-butene incorporation. This result could be anticipated from the 15-s pulse delay which was inadequate for the methyl resonances. Finally, definite splitting of the $\beta\delta^+$ resonance was also detected and is likely attributed to EBEE and BBEE tetrads.

The sum of the six triad areas provides the normalization factor which leads to final expressions for the triad distribution in terms of mole fractions:

$$TTA = \text{total triad area} = k([B] + [E]) = k([EBE] + [BBE] + [BBB] + [BEB] + [BEE] + [EEE]) \quad (44)$$

$$[EBE] = k[EBE]/TTA \quad (45)$$

$$[BBE] = k[BBE]/TTA, \text{ etc.} \quad (46)$$

Table IV
Triad Distributions As Measured by Methods A, B-1, and B-2 for Hydrogenated Polybutadienes HB-1, HB-2, and HB-3

	HB-1, [B] = 0.163			HB-2, [B] = 0.361			HB-3, [B] = 0.584		
triad	method A	method B-1	method B-2	method A	method B-1	method B-2	method A	method B-1	method B-2
[EBE]	0.099	0.098	0.099	0.093	0.093	0.093	0.039	0.043	0.037
[BBE]	0.058	0.054	0.054	0.193	0.190	0.190	0.246	0.249	0.249
[BBB]	0.005	0.011	0.010	0.076	0.078	0.078	0.306	0.292	0.298
[BEB]	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
[BEE]	0.255	0.250	0.252	0.379	0.376	0.376	0.324	0.334	0.323
[EEE]	0.584	0.586	0.586	0.259	0.263	0.263	0.086	0.088	0.088

Direct Area Measurements for Triads EBE, BBE, and BBB from $\alpha\delta^+$(EBEE), $\alpha\delta^+$(BBEE), and CH(BBB) in Region B

	HB-1		HB-2		HB-3	
triad	region B	average of B-1 and B-2	region B	average of B-1 and B-2	region B	average of B-1 and B-2
EBE	86.4	86.1	67.1	67.0	29.2	26.2
BBE	46.6	46.8	128.8	136.5	159.3	162.8
BBB	8.9	9.0	58.0	56.3	199.9	193.2

Table V
Triad Distributions, Average Sequence Lengths, Run Numbers, and Comonomer Mole Fractions for a Series of Hydrogenated Polybutadienes and Ethylene–1-Butene Copolymers from an Average of Methods B-1 and B-2

	hydrogenated polybutadienes			ethylene–1-butene copolymers			
	HB-1 43-5	HB-2 43-10	HB-3 43-15	EB-1 16-1	EB-2 16-7	EB-3 16-8	EB-4 16-29
[EBE]	0.099	0.093	0.040	0.020	0.049	0.065	0.100
[EBB]	0.054	0.190	0.249	0.002	0.012	0.017	0.029
[BBB]	0.010	0.078	0.295	0.000	0.006	0.006	0.013
[BEB]	0.000	0.000	0.000	0.001	0.009	0.015	0.028
[BEE]	0.251	0.376	0.329	0.039	0.092	0.118	0.175
[EEE]	0.586	0.263	0.088	0.939	0.833	0.779	0.655
$\bar{n}_E$	6.7	3.4	2.5	47.7	17.1	12.4	7.5
$\bar{n}_B$	1.3	1.9	3.6	1.04	1.2	1.2	1.2
run no.	12.6	18.8	16.4	2.05	5.5	7.4	11.5
100[B]	16.3	36.1	58.4	2.13	6.6	8.8	14.3

From these triad sequence mole fractions, we can derive a few secondary molecular structural parameters such as the mole percent 1-butene incorporated.

$$\text{mol \% [B]} = k[\text{B}] \times 100/\text{TTA} \quad (47)$$

The run number per 100 structural units as defined by Harwood[9] is

$$\bar{N} = kN \times 100/\text{TTA} = ([\text{EBE}] + \tfrac{1}{2}[\text{EBB}]) \times 100 \quad (48)$$

and the average comonomer sequence lengths are given by

$$\bar{n}_B = [\text{B}]/N \quad (49)$$

and

$$\bar{n}_E = [\text{E}]/N \quad (50)$$

If intensities of the end group carbons are also available, one can determine directly the degree of polymerization as well as other similar molecular parameters such as those mentioned above for an average polymer chain. These secondary molecular parameters are useful in probing physical properties of copolymer systems. For example, if the values of [B] and N are approximately the same, then the 1-butene units in the copolymer must occur principally as isolated branches. Details concerning this aspect of the ethylene–1-butene system will be reported separately. The triad distributions, run numbers, and average comonomer sequence lengths for all of the polymers listed in Table I are given in Table V.

Although the triad distribution leads to a complete characterization in terms of the molecular parameters mentioned above, the higher order tetrad distribution may be of interest either in statistical studies or in certain structure studies. A direct, independent determination of each of the 10 possible tetrads from the carbon-13 NMR spectral data is not feasible for the same reasons the triad analysis was so elusive; however, if one evokes the following necessary relationships between triads and tetrads, a quantitative identification of only a few tetrads can lead to the complete set

$$[\text{EEEE}] + [\text{BEEE}]/2 = [\text{EEE}] \quad (51)$$

$$[\text{BEEE}] + 2[\text{BEEB}] = [\text{BEE}] \quad (23)$$

$$[\text{EBEE}] + [\text{EBEB}] = 2[\text{EBE}] \quad (52)$$

$$[\text{BBEE}] + [\text{BBEB}] = [\text{BBE}] \quad (53)$$

$$[\text{EBEB}] + [\text{BBEB}] = 2[\text{BEB}] \quad (54)$$

$$[\text{EBEE}] + [\text{BBEE}] = [\text{BEE}] \quad (55)$$

$$[\text{BBBE}] + 2[\text{EBBE}] = [\text{BBE}] \quad (56)$$

and

$$[\text{BBBE}] + 2[\text{BBBB}] = 2[\text{BBB}] \quad (57)$$

To solve for the complete set of 10 tetrads, it is helpful to divide the eight necessary relationships listed above into three groups. The first group contains eq 51 and 23. Since there are three unknown variables, [EEEE], [BEEE], and [BEEB], involved, we need to identify only one of these three tetrad sequences independently. In this case eq 14 is chosen because $\gamma\gamma$(BEEB) is the best resolved peak among the resonances in region C. Equations 52–55 are in the second group for quantifying [EBEE], [BBEE], [EBEB], and [BBEB]. Only three of the four equations are independent; thus, once again, an independently

identified tetrad is needed among the four. Tests show

$$\alpha\delta^+(\text{EBEE}) = k[\text{EBEE}] \quad (58)$$

to be the most suitable choice. Finally, we have eq 56 and 57 to combine with yet another needed independent identification to form the third group. In this case $\alpha\alpha$-(EBBE) proves to be the best choice in region A:

$$\alpha\alpha(\text{EBBE}) = k[\text{EBBE}] \quad (59)$$

With only the three additional measurements discussed above, the triad analysis can be extended to a complete set of tetrads. Other direct tetrad measurements are possible as the $\alpha\alpha$ carbons, the $\alpha\gamma$ and $\alpha\delta^+$ carbons, and the $\gamma\gamma$ and $\gamma\delta^+$ carbons are clearly associated with tetrad sequences. It is better, however, to restrict the tetrad measurements to distinct, well-defined resonances as errors introduced from any single meassurement are carried over into the determination of the rest.

The quantitative methods presented in this study were designed to minimize errors arising from line broadening, uncertainties in configurational assignments, peak overlap, phasing, and differences in line widths. The utilization of broad spectral regions with complete, collective assignments and appropriate well-defined single resonances have eliminated many of these problems and has led to quantitative results which are internally consistent. When larger diameter probes are used, there may be a loss of spectral resolution. In such cases, it is likely that regions C and D will not be well separated. As a result, one should not utilize either methods A or B but combine regions C and D into one collective area. Equations 3c, 8, 9d, and 19, along with those describing regions C and D, can be used to determine more accurately a triad distribution.

A triad analysis is all that is needed to determine relative comonomer concentrations, average sequence lengths, and run numbers; all can be accurately obtained for the ethylene–1-butene copolymers. A tetrad distribution is available from the carbon-13 NMR data but will generally not be so accurate as the triad distribution as a further delineation of closely spaced resonances is required. With this reliable quantitative information, the polymer chemist is in a position to correlate various structural moieties with the observed density, flexural modulus, and other physical properties.

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Synthetic Polyampholytes. 2. Sequence Distribution in Methacrylic Acid–(Dimethylamino)ethyl Methacrylate Copolymers by ^{13}C NMR Spectroscopy†

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ABSTRACT: The ^{13}C NMR spectra of methacrylic acid–(dimethylamino)ethyl methacrylate copolymers in NaOD solution show a triad structure which is due solely to a copolymeric distribution without any tacticity effect for the carbonyl pattern (ionized acid or ester group). This permits assignments and sequence measurements. Polyampholytes prepared by radical-initiated copolymerization have a slight alternating tendency. Polyampholytes obtained by hydrolysis of poly[(dimethylamino)ethyl methacrylate] in concentrated sulfuric acid have a blocklike distribution of acid sequences which passes through a maximum as their acid content F_A is increased. Alkaline-hydrolyzed polyampholytes (2-propanol/KOH/H_2O in excess) also show a slight tendency to have a blocklike structure, which is greater in the beginning of the hydrolysis and tends toward randomness as the reaction progresses. Solubilities and apparent pKs of the polyelectolytes are discussed in terms of their microstructures.

Introduction

^{13}C NMR spectroscopy is an effective technique for measuring, or at least estimating, the triad composition in a copolymer: the differential nuclear Overhauser effect (NOE) enhancement is approximately equal for similar carbons within different types of chemical sequences.[1] It is also generally admitted that for nonprotonated carbons with restricted mobilities like in polymers, the residual spin–lattice relaxation times (T_1) are of the same order.[1] These assumptions, even if not exactly true as shown by Klesper et al.[2] for the methacrylic acid–methyl methacrylate copolymers (no difference detected in the NOE of COOH and $COOCH_3$ but differences in T_1), are the basis of studies of copolymer structures by ^{13}C NMR spectroscopy.

Very few NMR studies have been devoted to synthetic polyelectrolytes in aqueous solution. This is due to the insufficient definition of resonance signals that is generally obtained due to the large number of compositional–con-

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