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^{13}C NMR Spectra of Methyl-Substituted 1,4-*trans*-Polybutadienes. 2. Spectra of Several Copolymers

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Received January 20, 1984

ABSTRACT: The ^{13}C NMR spectra (recorded at 25.2 MHz) of ten diene copolymers having a 1,4-trans structure obtained by inclusion polymerization in perhydrotriphenylene (PHTP) are discussed. Monomers were chosen among butadiene, isoprene, *trans*-pentadiene, *trans*-2-methylpentadiene, 4-methylpentadiene, and 2,3-dimethylpentadiene. Assignments were made at the dyad and triad level, also taking into account the possibility of inversions of the monomer units. An appropriate set of parameters is used to compute chemical shift values for the various sequences, which were found to be in excellent agreement with experimental values.

The first of our articles published in this issue (hereafter called part 1)[1] describes a method of analysis of ^{13}C NMR spectra of methyl-substituted 1,4-*trans*-polybutadienes and discusses the spectra of a number of homopolymers obtained by inclusion polymerization in perhydrotriphenylene (PHTP). This second article extends the discussion to an extensive series of diene copolymers obtained by the same technique.

For a general discussion of this series of products and the criteria of interpretation, the reader should refer to part 1. Concerning the nomenclature, further specification is required beyond what is reported in Table I of part 1. Due to the less rigorous selection rules existing in inclusion copolymerization in comparison to homopolymerization, the occurrence of head-to-head and tail-to-tail sequences must be taken into account. As a consequence we found it convenient to use a different symbol for the monomer units inserted in the chain in the opposite way: letters marked with an asterisk (I*, P*, etc.) denoted monomer units presenting the atom C4 at the left and C1 at the right.

The copolymers dealt with in this article were obtained from pairs of monomers chosen among butadiene, isoprene, *trans*-pentadiene, *trans*-2-methylpentadiene, 4-methylpentadiene, and 2,3-dimethylbutadiene. The amount of information contained in their spectra depends on the number of nonequivalent methyl groups present in the monomer units and on the occurrence of inversions. Thus, copolymers showing chiefly a head-to-tail structure will be first examined; then those based on butadiene and dimethylbutadiene will be discussed. Finally, we will present two examples of complex spectra for which an extended use of the parameter set previously reported[1] is necessary.

It should be stressed that our examination is focused on the interpretation of the spectra. Signal intensities are considered only marginally; a thorough discussion of this aspect, and in general a discussion of copolymerization in PHTP, will be undertaken in a further article.[2]

Results and Discussion

Poly(2-methylpentadiene-*co*-4-methylpentadiene). This copolymer, hereafter called TF copolymer, was first obtained by the accidental partial isomerization of a sample of 2-methylpentadiene[3] and for a long time was one of the few copolymers obtained in inclusion compounds. Even today the complete definition of its spectrum and the absence of side structures make this product worthy of particular attention. Our discussion will be particularly detailed as an example of the method of analysis used throughout this paper.

A series of copolymers was prepared, ranging from 20 to 80% of each monomer. Their ^{13}C NMR spectra (Figure 1) present 37 signals, of which 16 at low field are assigned to the unsaturated carbons C2 and C3 of both monomer units. The remaining 21 signals, ranging from 16 to 54 ppm, can easily be divided into four groups on the basis of the off-resonance decoupled spectrum: the 9 signals from 16 to 27 ppm are attributed to methyls C2′ and C4′ of the monomer unit deriving from 2-methylpentadiene (hereafter denoted by C2′-T and C4′-T) and to geminal

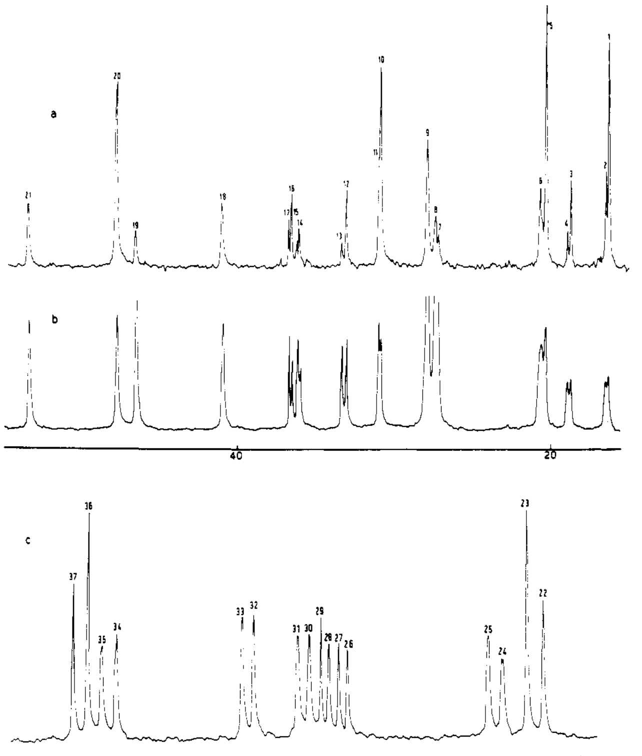

Figure 1. ^{13}C NMR spectrum of TF copolymer: (a) saturated carbons in a 73% T sample and (b) in a 24% T sample; (c) unsaturated carbons in a 45% T sample (the spectrum of the unsaturated carbons in the 73% sample has been reported in Figure 2 of part 1).

methyls C4′-F, signals 10–13 are attributed to the tertiary carbon C4-T, signals 14–17 are assigned to quaternary carbon C4-F, and signals 18–21 are assigned to methylene carbons C1-F and C1-T.

By comparison with the homopolymers it was possible to assign with certainty signals 1, 5, and 8 to carbons C2′-T and C4′-T of the triad TTT and to carbon C4′-F of dyad –FF, respectively. It was further observed that the sum of the intensities of peaks 1, 2, 3, and 4 equals that of peaks 5 and 6 in all the copolymers examined, whatever their composition. These two groups are therefore to be attributed to C2′-T in the four T-centered triads (TTT, TTF, FTT, and FTF) and to C4′-T in the T-centered dyads (–TT and –TF). More detailed information can be obtained from an examination of the intensity ratios within each group of signals. It is worth noting that if we take into consideration only the sequences centered on a given monomer instead of all possible sequences, particularly simple expressions are obtained: the relative concentration of dyads varies linearly with copolymer composition, while that of the triads can be expressed by a quadratic formula (for example, x^2 for the sequence TTT, $x(1-x)$ for the two triads TTF and FTT, and $(1-x)^2$ for the triad FTF). This offers definite advantages: the order of the expressions is reduced by one degree, linear and quadratic for dyads and triads instead of quadratic and cubic; the field of validity of the treatment is extended, no longer being limited to the case of a Bernoulli distribution (ideal copolymer) but also applicable to a first-order Markov distribution. Moreover, a better agreement between calculated and experimental data is obtained, because signals due to the same carbon are directly compared, thus reducing differences in relaxation times and NOE's.

On this basis peak 4 is attributed to C2′-T in FTF and peak 6 to C4′-T in –TF. For the assignment of peak 2 to TTF and of peak 3 to FTT it is advisable to compare the entire structure of the triads and evaluate the effects of the substituents on the italicized carbon:

$$\mathrm{-CH_2C(CH_3){=}CHCH(CH_3)CH_2C(\mathit{C}H_3){=}}$$
$$\mathrm{CHCH(CH_3)CH_2C(CH_3){=}CHCH(CH_3)\text{-}}$$
TTT

$$\mathrm{-CH_2CH{=}CHC(CH_3)_2CH_2C(\mathit{C}H_3){=}}$$
$$\mathrm{CHCH(CH_3)CH_2C(CH_3){=}CHCH(CH_3)\text{-}}$$
FTT

$$\mathrm{-CH_2C(CH_3){=}CHCH(CH_3)CH_2C(\mathit{C}H_3){=}}$$
$$\mathrm{CHCH(CH_3)CH_2CH{=}CHC(CH_3)_2\text{-}}$$
TTF

With respect to TTT, FTT has an extra methyl at a distance of three bonds, analogous to a γ-substituent in our scheme, while TTF shows the lack of a methyl group at a distance of five bonds ($-\epsilon$ effect). Though no set of parameters relating to the methyl carbons has been determined, it seems reasonable to suppose that a considerable deshielding effect ($\Delta\nu = +2.40$) is to be attributed to the presence of a further methyl bonded to a γ carbon, and a weak effect of the opposite sign to the presence of a substituent on an ϵ carbon (–0.2). It follows that we can be reasonably confident in assigning peak 2 to TTF and peak 3 to FTT.

Signals 7, 8, and 9 are due to *gem*-C4′-F arranged in various sequences. This part of the analysis differs from the attributions anticipated in earlier publications of ours.[4,5] On the basis of intensities, we had attributed signal 7 to FFF, signal 8 to TFF, and signal 9 to –FT. A more detailed examination has instead revealed that FFF corresponds to signal 8 (which coincides with the peak of the homopolymer). The attribution of signal 7 is harder to decide. It must be borne in mind that in the copolymer sequences the two *gem*-methyls C4′-F are no longer equivalent as they are in the homopolymer but diastereotopic: in fact they undergo the influence of the asymmetric carbon of monomer unit T and should therefore be indicated as C4′-F and C4″-F. On the basis of the intensities and the chemical shift differences (the distance between signals 7 and 8 is only 0.2 ppm, while that between signals 8 and 9 is 0.5 ppm), we feel that the most plausible explanation is the following: peak 7 corresponds to one of the methyls, e.g., C4″-F, of triad TFF; peak 8 is due to the other methyl (C4′-F) of the same sequence TFF in addition to the two equivalent C4′-F of FFF; peak 9 contains both the methyls C4′ and C4″ of triads –FT.

Moving downfield we come to the carbon atoms of the main chain, starting with the tertiary C4-T. In the region between 30.7 and 30.9 ppm we observe a peak which, according to the copolymer composition and to recording conditions, either shifts slightly or splits into two very close signals, which we will call signals 10 and 11, almost coincident with the homopolymer signal (30.75 ppm).[6] This system can be assigned to the triads –TT; more precisely, signal 10 corresponds to TTT and signal 11 to FTT (this latter signal prevails in samples with a low T content, which explains the small variation of the chemical shift observed in this case). The other two signals of C4-T, sharply separated from the preceding ones and close to each other (peaks 12 and 13), are attributed by their intensity to TTF and FTF, respectively.

The arrangement of signals 10–13 is similar to that observed for C2′-T (signals 1–4): starting from high field, in a polymer rich in T we observe an intense peak, a medium-sized peak very close to it, another medium-intensity

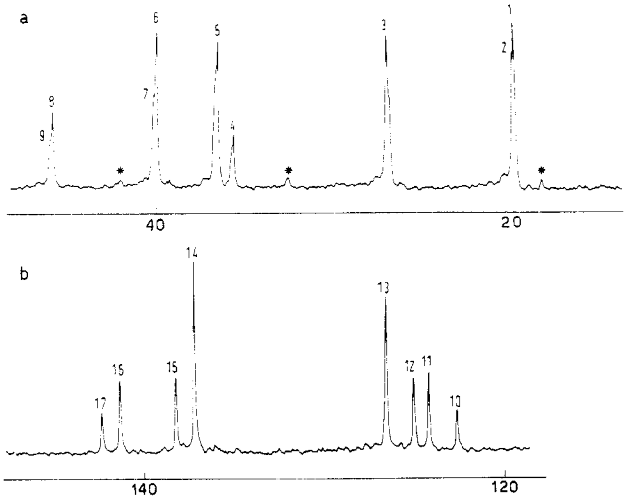

Figure 2. ^{13}C NMR spectrum of PF copolymer containing 67% P units: (a) saturated carbons and (b) unsaturated carbons. Asterisks mark signals due to PP* sequences.

peak at a considerable distance, and lastly a weak peak close to the preceding one. Nonetheless the attribution of the central peaks is the opposite: TTF and FTT for peaks 2 and 3 and FTT and TTF for peaks 11 and 12, because of the different position of the carbon within the monomer unit. As a matter of fact, on moving from TTT to TTF, C4-T no longer undergoes the strong shielding effect of a substituent in β position ($|\Delta\nu| \simeq 2$ ppm), while the passage from TTT to FTT or from TTF to FTF involves only variations of δ parameters, which of course are much smaller.

The assignment of peaks 14–17 to quaternary carbon C4-F is given by off-resonance decoupling experiments. The four signals fall within 0.65 ppm and form two almost equally spaced pairs ($\Delta\nu = 0.1$ and 0.15 ppm).

Following the usual intensity criteria, peak 15 is attributed to FFF and peak 16 to TFT, while for the attribution of peaks 14 and 17 comparison with the spectrum of the copolymer pentadiene–4-methylpentadiene (PF copolymer) is useful. (See Figure 2.) In a sample of this product with a P/F ratio equal to 2:1 we observe a rather wide isolated signal at 35.93 ppm due to C4-F, slightly upfield with respect both to the unknown signal 14 ($\Delta\nu = 0.05$ ppm) and to that of the FFF triad in the homopolymer ($\Delta\nu = 0.15$ ppm). The sole difference between sequences TFF and PFF consists in the presence of a C2′ methyl in the preceding monomer unit, six bonds away from C4-F and hence having no effect on the spectrum. Signal 14 at 35.97 ppm is thus attributed to TFF, and by exclusion peak 17 at 36.62 ppm is attributed to FFT.

The remaining four signals of the saturated zone are due to the C1 methylenes of both monomer units. These are widely spaced dyad signals sensitive to the preceding, and not to the following, monomer unit. Correspondence to the homopolymer signal permits us to state that peak 19 is due to FF– and peak 20 to TT–. The abnormal chemical shift of signal 21 is justified by the intense crowding of methyls around C1-T in FT–: there is one α' methyl in the same monomer unit and there are two in position α in the preceding monomer unit. In its turn, peak 18 has a chemical shift very close to that of C1-F in PF copolymer (40.85 as against 40.47 ppm) and can thus be attributed to C1-F in the TF– sequence.

The foregoing discussion can be expressed in quantitative terms by using the scheme of additive contributions and the set of parameters given in part 1. Table I gives the list of parameters used for each sequence and compares computed with experimental data.

Table I
Observed and Calculated Chemical Shifts in TF Copolymer

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
		Saturated Carbons		
1	C2′ TTT		16.32	
2	C2′ TTF		16.45	
3	C2′ FTT		18.70	
4	C2′ FTF		18.92	
5	C4′ -TT		20.30	
6	C4′ -TF		20.60	
7	C4″ TFF		27.12	
8	C4′ TFF + FFF		27.30	
9	C4′ + C4″ -FT		27.81	
10	C4 TTT	$\mathrm{T}, \beta'_{\mathrm{T}}, \beta_{\mathrm{T}}, \delta_{\mathrm{T}\beta}, \delta'_{\mathrm{T}\beta'}$	30.75	30.75
11	C4 FTT	$\mathrm{T}, \beta'_{\mathrm{T}}, \beta_{\mathrm{T}}, \delta_{\mathrm{T}\beta}, \mathrm{G}\delta'_{\mathrm{T}\beta'}$	30.85	30.90
12	C4 TTF	$\mathrm{T}, \beta'_{\mathrm{T}}, \mathrm{G}\delta_{\mathrm{T}}, \delta'_{\mathrm{T}\beta'}$	32.95	33.05
13	C4 FTF	$\mathrm{T}, \beta'_{\mathrm{T}}, \mathrm{G}\delta_{\mathrm{T}}, \mathrm{G}\delta'_{\mathrm{T}\beta'}$	33.27	33.20
14	C4 TFF	$\mathrm{Q}, \mathrm{G}\delta_{\mathrm{Q}}, \delta'_{\mathrm{Q}}$	35.97	35.95
15	C4 FFF	$\mathrm{Q}, \mathrm{G}\delta_{\mathrm{Q}}, \mathrm{G}\delta'_{\mathrm{Q}}$	36.07	36.10
16	C4 TFT	$\mathrm{Q}, \beta_{\mathrm{Q}}, \delta_{\mathrm{Q}\beta}, \delta'_{\mathrm{Q}}$	36.46	36.45
17	C4 FFT	$\mathrm{Q}, \beta_{\mathrm{Q}}, \delta_{\mathrm{Q}\beta}, \mathrm{G}\delta'_{\mathrm{Q}}$	36.62	36.60
18	C1 TF–	$\alpha, \gamma_{\alpha}, \mathrm{G}\gamma'$	40.92	40.80
19	C1 FF–	$\mathrm{G}\alpha, \mathrm{G}\gamma'$	46.45	46.40
20	C1 TT–	$\alpha, \alpha'_{\alpha}, \gamma_{\alpha}, \gamma'_{\alpha\alpha'}$	47.66	47.70
21	C1 FT–	$\mathrm{G}\alpha, \alpha', \gamma'_{\alpha\alpha'}$	53.27	53.30
		Unsaturated Carbons		
22	C2 FFT	$\mathrm{G}\beta, \mathrm{G}\beta', \delta'_{\mathrm{G}\beta'}$	121.70	121.70
23	C2 FFF	$\mathrm{G}\beta, \mathrm{G}\beta'$	121.42	121.40
24	C2 TFT	$\mathrm{G}\beta, \mathrm{G}\beta', \delta'_{\mathrm{G}\beta'}, \delta_{\beta}$	123.47	123.55
25	C2 TFF	$\mathrm{G}\beta, \mathrm{G}\beta', \delta_{\beta}$	124.16	124.25
26	C2 FTT	$\mathrm{T}, \beta'_{\mathrm{T}}, \mathrm{G}\beta_{\mathrm{T}}, \delta'_{\mathrm{T}\beta'}$	130.61	130.60
27	C2 FTF	$\mathrm{T}, \beta'_{\mathrm{T}}, \mathrm{G}\beta_{\mathrm{T}}$	131.00	131.05
28	C2 TTT	$\mathrm{T}, \beta'_{\mathrm{T}}, \beta_{\mathrm{T}}, \delta'_{\mathrm{T}\beta'}, \delta_{\mathrm{T}\beta}$	131.45	131.45
29	C2 TTF	$\mathrm{T}, \beta'_{\mathrm{T}}, \beta_{\mathrm{T}}, \delta_{\mathrm{T}\beta}$	131.81	131.90
30	C3 TTF	$\alpha, \alpha'_{\alpha}, \gamma'_{\alpha\alpha'}, \epsilon'_{\alpha'\gamma'}$	132.32	132.35
31	C3 TTT	$\alpha, \alpha'_{\alpha}, \gamma'_{\alpha\alpha'}, \gamma_{\alpha\alpha'}, \epsilon'_{\alpha'\gamma'}$	132.85	132.90
32	C3 FTF	$\alpha, \alpha'_{\alpha}, \mathrm{G}\gamma'_{\alpha'}$	134.84	134.85
33	C3 FTT	$\alpha, \alpha'_{\alpha}, \mathrm{G}\gamma'_{\alpha'}, \gamma_{\alpha\alpha'}$	135.34	135.40
34	C3 TFF	$\mathrm{G}\alpha, \gamma'_{\mathrm{G}\alpha}$	141.25	141.25
35	C3 TFT	$\mathrm{G}\alpha, \gamma'_{\mathrm{G}\alpha}, \gamma_{\mathrm{G}\alpha}$	141.87	141.90
36	C3 FFF	$\mathrm{G}\alpha, \mathrm{G}\gamma'$	142.50	142.50
37	C3 FFT	$\mathrm{G}\alpha, \mathrm{G}\gamma', \gamma_{\mathrm{G}\alpha}$	143.22	143.15

Sixteen well-spaced signals are visible between 120 and 145 ppm in the unsaturated carbon region. Their straightforward attribution is made at triad level. The spectrum is divisible into four subspectra, each of four signals, due respectively to C2-F, C2-T, C3-T, and C3-F. The following attributions are immediate: for carbon C2, triad FFF corresponds to peak 23, TFT to peak 24, FTF to peak 27, and TTT to peak 28; for carbon C3, TTT corresponds to peak 31, FTF to peak 32, TFT to peak 35, and FFF to peak 36. The other eight signals were attributed by computation of the spectrum by means of the additive contributions. A discussion of the assignment of signals 22–25 has already been given in part 1.

The spectrum of the unsaturated part presents considerable symmetry as regards the arrangement of signals. In particular, the shielding and deshielding effects are almost exactly inverted when the carbon under observation is exchanged. As a matter of fact, C2-F in FFT gives rise to the highest field signal and, in the same sequence, C3-F gives the lowest field signal, with a shift of 21.5 ppm. On the contrary, the effect is minimal with triad TTF, where the difference between C2 and C3 is only 0.5 ppm.

We conclude this examination by emphasizing that the spectrum of the copolymer is interpreted entirely on the basis of the pure 1,4-trans head-to-tail structure. There is no evidence as to the presence of secondary structures such as 1,2, 3,4, or 1,4-cis units, of cyclic units, or of head-to-head:tail-to-tail sequences. As regards this last

Table II
Observed and Calculated Chemical Shifts in PT Copolymer

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
		Saturated Carbons		
1	C2′ T		16.29	
2	C2′ T		16.40	
3	C4′ P		19.97	
4	C4′ T		20.30	
5	C4′ T		20.41	
6	C4′ T		20.60	
7	C4 –TT	$T, \beta_T, \beta'_T, \delta_{T\beta}, \delta'_{T\beta'}$	30.75	30.75
8	C4 –TP	$T, \beta'_T, \delta_T, \delta'_{T\beta'}$	32.92	32.90
9	C4 –PT	$T, \beta_T, \delta_{T\beta}, \delta'_T$	34.59	34.65
10	C4 –PP	T, δ_T, δ'_T	36.83	36.80
11	C1 PP–	α, γ'_α	40.32	40.30
12	C1 TP–	$\alpha, \gamma_\alpha, \gamma'_\alpha$	40.63	40.60
13	C1 PT–	$\alpha, \alpha'_\alpha, \gamma'_{\alpha\alpha'}$	47.65	47.70
13	C1 TT–	$\alpha, \alpha'_\alpha, \gamma_{\alpha\alpha'}, \gamma'_{\alpha\alpha'}$	47.65	47.70
		Unsaturated Carbons		
14	C2 PPT	$\beta, \beta', \delta'_{\beta'}$	126.00	126.05
15	C2 TPT	$\beta, \beta', \delta_\beta, \delta'_{\beta'}$	126.28	126.30
16	C2 PPP	β, β'	126.39	126.40
17	C2 TPP	$\beta, \beta', \delta_\beta$	126.61	126.65
18	C2 PTT	$T, \beta_T, \beta'_T, \delta'_{T\beta'}$	131.27	131.25
19	C2 TTT	$T, \beta_T, \beta'_T, \delta_{T\beta}, \delta'_{T\beta'}$	131.45	131.45
20	C2 PTP	T, β_T, β'_T	131.67	131.70
21	C2 TTP	$T, \beta_T, \beta'_T, \delta_{T\beta}$	131.87	131.90
22	C3 TTP	$\alpha, \alpha'_\alpha, \gamma'_{\alpha\alpha'}, \epsilon'_{\alpha'\gamma'}$	132.29	132.35
23	C3 PTP	$\alpha, \alpha'_\alpha, \gamma'_{\alpha\alpha'}$	132.48	132.60
24	C3 TTT	$\alpha, \alpha'_\alpha, \gamma'_{\alpha\alpha'}, \gamma_{\alpha\alpha'}, \epsilon'_{\alpha'\gamma'}$	132.89	132.90
25	C3 PTT	$\alpha, \alpha'_\alpha, \gamma'_{\alpha\alpha'}, \gamma_{\alpha\alpha'}$	133.08	133.15
26	C3 TPP	$\alpha, \gamma'_\alpha, \epsilon'_{\alpha\gamma'}$	136.92	136.90
27	C3 PPP	α, γ'_α	137.18	137.15
28	C3 TPT	$\alpha, \gamma'_\alpha, \gamma_\alpha, \epsilon'_{\alpha\gamma'}$	137.31	137.25
29	C3 PPT	$\alpha, \gamma'_\alpha, \gamma_\alpha$	137.54	137.50

aspect, our parameterization scheme makes it possible to predict the position of the resonances of the atoms in the chain in all possible sequences: for example, in dyad T*F, carbon C1-T should have a chemical shift of 39.85 ppm and C1-F of 31.45 ppm. No significant peak was however observed in these position within the limits of the sensitivity of the experiment.

Poly(pentadiene-*co*-2-methylpentadiene). The spectrum of PT copolymer shows 29 signals, 6 of which are attributed to methyls, 7 to main-chain saturated carbons, and 16 to unsaturated carbons (Table II).

The discussion reported in this section—and the following ones—is essentially qualitative, while the computational aspect can be drawn from the table.

Signals 1 and 2 are due to carbon C2′-T: more precisely, signal 1 corresponds to the homopolymer sequence TTT and signal 2 to copolymer sequences that cannot be distinguished from each other. The coincidence with the homopolymer signals also assigns signal 3 to C4′-P in triad PPP and signal 4 to C4′-T in TTT. Signals 5 and 6 also belong to C4′ carbons in unidentified mixed sequences.

In the region between 30 and 37 ppm four well-separated signals are found, almost equidistant from each other; these are to be attributed to tertiary carbons C4-T of the dyads –TT (signal 7) and –TP (signal 8) and C4-P of dyads –PT (signal 9) and –PP (signal 10). The particular aspect of the spectrum is due to the presence of β'_T substituents (in –TT and –TP) and β_T (in –TT and –PT) and to the particular value of their respective parameters (β'_T being almost exactly twice β_T).

The following three signals are due to C1-P in PP– (signal 11) and TP– (signal 12) and to C1-T (signal 13): the dyad signals degenerate into a single rather wide peak in this last case.

Table III
Observed and Calculated Chemical Shifts in PF Copolymer

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
		Saturated Carbons		
1	C4′ P		20.00	
2	C4′ P		20.08	
3	C4′ F		27.38	
4	C4 FFF	$Q, G\delta'_Q, G\delta_Q$	35.93	36.10
	C4 FFP	$Q, G\delta'_Q, \delta_Q$	35.93	35.95
	C4 PFF	$Q, \delta'_Q, G\delta_Q$	35.93	35.95
	C4 PFP	Q, δ'_Q, δ_Q	35.93	35.80
5	C4 PPP	T, δ'_T, δ_T	36.82	36.80
	C4 PPF	$T, \delta'_T, G\delta_T$	36.82	36.95
	C4 FPP	$T, G\delta'_T, \delta_T$	36.82	36.95
	C4 FPF	$T, G\delta'_T, G\delta_T$	36.82	37.10
6	C1 PP–	α, γ'	40.34	40.25
7	C1 PF–	$\alpha, G\gamma'$	40.47	40.45
8	C1 FP–	$G\alpha, \gamma'$	46.24	46.20
9	C1 FF–	$G\alpha, G\gamma'$	46.37	46.40
		Unsaturated Carbons		
10	C2 FF–	$G\beta', G\beta$	122.41	122.40
11	C2 PF–	$G\beta', \beta$	123.98	123.95
12	C2 FP–	$\beta', G\beta$	124.84	124.85
13	C2 PP–	β', β	126.37	126.40
14	C3 PP–	α, γ'_α	137.17	137.10
15	C3 FP–	$\alpha, G\gamma'$	138.24	138.15
16	C3 PF–	$G\alpha, \gamma'_\alpha$	141.42	141.40
17	C3 FF–	$G\alpha, G\gamma'$	142.47	142.40

The structure of the unsaturated part of the spectrum is very similar to that of the TF copolymer already discussed. Here, too, the 16 signals are divided into four subspectra, each of four signals: peaks 14–17 are assigned to C2-P in the four possible triads, peaks 18–21 to C2-T, peaks 22–25 to C3-T, and peaks 26–29 to C3-P.

Unlike the FT copolymer, the spacing between signals is very small (each subspectrum occupying only 0.6–0.9 ppm). Assignment of single peaks was carried out on the basis of intensity considerations and by comparison with computed data.

Poly(pentadiene-*co*-4-methylpentadiene). Compared with those described above, this polymer presents a less detailed spectrum: at first sight, only six signals (equal to the number of independent saturated carbons in the two monomer units) appear to be present in the high-field zone and eight (i.e., double the number of dyads) in the low-field zone. In reality, taking into account slight splittings and the presence of a few shoulders, for which a reasonable explanation can be found, the main signals in the saturated zone amount to 9, in addition to three very small signals at 18.45, 32.95, and 42.65 ppm (Table III, Figure 2).

The methyl signal of pentadiene unit C4′-P appears split into two components very close to each other, the higher field one corresponding to sequence PPP and the lower field one to the mixed sequences –PF and FP–. The two *gem*-methyls C4′-F and C4″-F form a single, slightly deformed peak, practically insensitive to the microstructure of the copolymer.

Carbons C4-F and C4-P also give rise to one signal each, rather wide and deformed. The center of the signal does not correspond exactly to that of the homopolymer because of the superposition of unresolved resonances having a slightly different chemical shift and different intensity.

As regards C1, an interesting anomaly is found: the two signals very close to each other around 40 ppm do not belong to the same carbon arranged in different sequences but to carbons of different monomer units and must be attributed to C1-P in dyad PP– (signal 6) and to C1-F in dyad PF– (signal 7). Similarly, the two signals around 46

Table IV
Chemical Shift Differences (ppm) for Main-Chain Carbon Atoms in Various Sequences

atom	pentadiene carbons ν(FP–) – ν(PP–)	4-methylpentadiene carbons ν(FF–) – ν(PF–)
C1	5.90	5.90
C2	–1.53	–1.57
C3	1.07	1.05
C4	$\simeq$0	$\simeq$0

ppm are assigned to C1-P in FP– (signal 8) and to C1-F in FF– (signal 9). In other words, the position of the signal for C1 primarily depends on the type of $n - 1$ unit and not on the unit in which the carbon in question is inserted (n). This interpretation is quite reasonable, bearing in mind that C1 is strongly affected by substituent C4 of the adjacent $n - 1$ unit (α effect) and only marginally by the C4 of the same unit, which gives rise only to a γ' effect.

The low-field zone contains eight well-spaced signals, corresponding to the four dyads. In this case, too, we find a situation similar to that described with reference to C1. The dyads responsible for the signals are those of units $n - 1$ and n, while the following unit has no influence at all (the substituents on unit $n + 1$ might be responsible only for ϵ or more distant effects). This applies both to C2 and to C3.

Table IV provides a comparative examination of this effect on both saturated and unsaturated carbons. The absolute value of the difference in chemical shift between sequences FP– and PP– and between FF– and PF– for the various carbons decreases from C1 to C4 and is practically nil for the latter.

The three minor signals mentioned earlier are due to head-to-head (PP*) and tail-to-tail (P*P) pentadiene sequences. This attribution derives from comparison with the spectra of polypentadiene and of polyhexadiene:[8,9] the signal at 18.45 ppm corresponds to the one which Priola, Corno, and Cesca attribute to the adjacent methyl groups in the threo position (18.42 ppm in cationic polypentadiene); the signal at 32.95 ppm is due to the adjacent methylene carbons (32.91 ppm), and the signal at 42.65 ppm corresponds reasonably well to that of the sequence –$CH(CH_3)$–$CH(CH_3)$– with the substituents in the threo position (42.47 ppm). The content of hh and tt sequences is very small (1–2% of the total pentadiene units) but significantly larger than that present in homopolymers obtained by inclusion polymerization in PHTP (except for polyisoprene), in which the corresponding signals are not observable over the noise.

Poly(butadiene-*co*-pentadiene). An examination of the high-field region alone is not sufficient to indicate the existence of a true statistical copolymer: in fact it presents only four signals, coincident with those of the homopolymers and might be interpreted as a mixture of homopolymers or as a block copolymer. Unequivocal proof of the statistical nature of the copolymer comes from examination of the unsaturated-carbon spectrum, which contains seven signals, four more than those to be expected under the other structural hypotheses (Table V, Figure 3).

The small number of signals is due to coincidence between the resonances of sequences which are constitutionally different but locally indistinguishable, because of the small number of methyl substituents bound to the polybutadiene skeleton and of the distance between them.

Despite its deceptive simplicity the spectrum must be interpreted at the triad level, taking into account the possibility of inverted insertions of pentadiene units. Among the various causes that may produce such defects is deformation of the channel of the inclusion compounds, whose structure is already altered by the presence of two monomers of different shape. Another cause is the presence of a nonsubstituted monomer such as butadiene, which removes the interactions between substituents and allows the introduction of P* units (4–1 units instead of 1–4), giving rise to copolymer sequences of types BP*P, PBP*, etc. As regards the former of these causes, a clue to its efficiency, already found in the PF copolymer, is the presence of two weak signals only just above the noise level, at 18.45 and 42.66 ppm, attributed to the carbons C4′-P and C4-P in the threo PP* sequences (the third signal relating to C1-P, whose chemical shift is around 32.9 ppm, coincides with an intense signal and hence is not observable).

The presence of PP* sequences, even though in minimal quantity, leads one to suppose that BP* sequences are also present—which from a topochemical point of view should be more frequent. Unfortunately, we have no sure confirmation of their existence because of the considerable degeneration of the spectrum. The analysis that follows here nonetheless takes their existence into account.

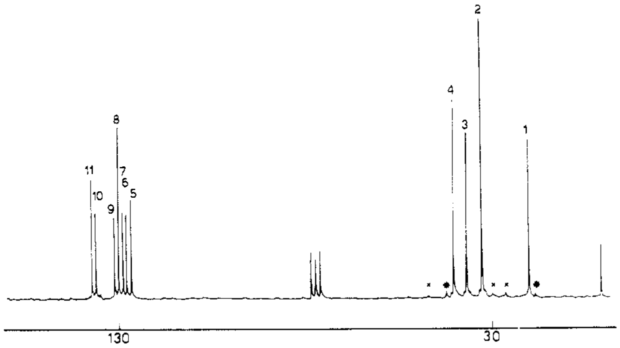

Figure 3. ^{13}C NMR spectrum of BP copolymer. Asterisks mark signals due to PP* sequences and ×'s those of PHTP impurity.

Table V
Observed and Calculated Chemical Shifts in BP Copolymer[a]

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
		Saturated Carbons		
1	C4′ P		20.00	
2	C1 BP–	γ', (δ')	32.74	32.70
	C1 P*P–	γ', δ, (δ')	32.74	32.70
	C1 BB–	(δ')	32.74	32.70
	C1 P*B–	δ, (δ')	32.74	32.70
3	C4 –PB	T, (δ'_T)	36.79	36.80
	C4 –PP	T, δ_T, (δ'_T)	36.79	36.80
4	C1 PP–	α, γ'_α, (δ'_α)	40.28	40.30
	C1 PB–	α, (δ'_α)	40.28	40.30
		Unsaturated Carbons		
5	C2 PP–	β', β	126.35	126.40
6	C2 BP–	β'	127.63	127.60
	C2 P*P–	β'	127.63	127.60
7	C2 PBB	β	128.66	128.65
	C2 PBP	β	128.66	128.65
8	C2 BBB		129.85	129.85
	C2 P*BB		129.85	129.85
	C2 BBP		129.85	129.85
	C2 P*BP		129.85	129.85
	C2 PBP*	β, γ'	129.85	129.70
9	C3 PBB	γ'	130.89	130.90
	C3 PBP	γ'	130.89	130.90
10	C3 BP–	α	136.05	136.05
	C3 P*P–	α	136.05	136.05
11	C3 PP–	α, γ'_α	137.14	137.15

[a] For signals presenting the sequence PP*, see text.

In the low-field spectrum the pairs of signals 5 and 6 and 10 and 11 are due respectively to C2-P and C3-P; signals 5 and 11 coincide with the peaks of the homopolymer (triad PPP) and contain a contribution from triad PPB, while signals 6 and 10 correspond to the sequence

$$\text{-CH=CHCH}_2\text{CH}_2\text{CH=CHCH(CH}_3\text{)CH}_2\text{CH=CH-}$$

which represents the structure common to triads BPB, BPP, P*PB, and P*PP. In their turn, triads BPP* and possibly, P*PP* and PPP* should give rise to weak signals at 129.23, 134.17, and 135.29 ppm, not emergent above background.[8]

The three signals 7, 8, and 9, where signals 7 and 9 are of the same intensity, derive from the unsaturated carbons of the butadiene units. For reasons of symmetry the six independent triads theoretically give rise to 9 signals, which can be grouped as follows: carbon C2-B of triads PBP and PBB resonates at 128.66 ppm (peak 7) and carbon C3-B of the same triads resonates at 130.89 ppm (peak 9); carbon C2-B (and its symmetric equivalent C3-B) of triads BBB and P*BP as well as carbons C2-B and C3-B (practically equivalent due to degeneration) of triad BBP gives rise to peak 8 (129.85 ppm). The signal of symmetric triad PBP* also contributes to peak 8 because of accidental compensation between the β (−1.20 ppm) and γ' (+1.05 ppm) parameters. A direct evaluation of this can immediately be obtained from the spectrum by observing the spacing between signals 8 and 9 (corresponding to the γ' effect) and between signals 8 and 7 (corresponding to the β effect).

In the high-field zone it should be noted that the homopolymeric signals 2 and 4 contain substantial contributions from copolymer sequences: peak 2 in fact includes the resonances of C1-P in BP– and P*P– and of C1-B in BB– and P*B– (this latter may also be described as C4-B in –BP), while both C1-P of PP– and C1-B of PB– contribute to peak 4.

Poly(butadiene-*co*-isoprene). The saturated-carbon region is in this case more detailed than that of the olefinic carbons, containing 9 out of a total of 14 signals. Six homopolymer signals are found, 5 due to isoprene (C2′-I, C4-I head-to-tail, C4-I tail-to-tail, C1-I head-to-head, and C1-I head-to-tail) and one signal due to butadiene (Table VI).

Of the four signals to be expected for the mixed dyads BI (or I*B) and IB (or BI*), three have been identified in peaks 3 (C4-I in –IB), 5 (C1-B in I*B– or the equivalent C4-B in –BI), and 7 (C1-B in IB– or C4-B in –BI*), while the fourth signal (C1-I in BI–) coincides with the homopolymer signal 9 (C1-I in II–).

The intensity of signals 2 and 8 gives us a rough idea of the proportion of head-to-head and tail-to-tail sequences existing with respect to head-to-tail sequences: it is much the same as that found in homopolymerization of isoprene under analogous conditions.

The olefinic region gives five signals: C3-I and C2-B (and its equivalent C3-B) produce only two peaks (peaks 10 and 11), while C2-I splits into three signals (peaks 12–14), the last of which contains the head-to-tail homopolymer triads.

The ^{13}C NMR spectrum of 1,4-trans IB copolymers obtained in the presence of coordination catalysts is reported by Lobach et al.;[10] the chemical shifts and assignments coincide with those given by us.

Poly(butadiene-*co*-4-methylpentadiene). Unlike copolymers PF and BP, already described, this and BT copolymer, which is next described, present no signs of inversion of the monomer units.

Table VI
Observed and Calculated Chemical Shifts in BI Copolymer

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
	Saturated Carbons			
1	C2′ I		16.07	
2	C4 –II	β', β	26.74	26.70
3	C4 –IB	β'	28.18	28.15
4	C4 –II*	β', $\gamma_{\beta'}$	28.28	28.25
5	C1 I*B–	β	31.31	31.25
6	C1 BB–		32.75	32.70
7	C1 IB–	γ	32.85	32.80
8	C1 I*I–	α', $\beta_{\alpha'}$	38.50	38.50
9	C1 BI–	α'	39.75	39.70
	C1 II–	α', $\gamma_{\alpha'}$	39.75	39.70
	Unsaturated Carbons			
10	C3 I*IB	α', $\delta'_{\alpha'}$	124.12	123.70
	C3 I*II	α', $\gamma_{\alpha'}$, $\delta'_{\alpha'}$	124.12	123.90
	C3 I*II*	α', $\delta'_{\alpha'}$, δ	124.12	123.95
	C3 BIB	α'	124.12	123.95
	C3 IIB	α'	124.12	123.95
	C3 BII	α', $\gamma_{\alpha'}$	124.12	124.15
	C3 III	α', $\gamma_{\alpha'}$	124.12	124.15
	C3 BII*	α', δ	124.12	124.20
	C3 III*	α', δ	124.12	124.20
11	C2 BBI	δ'	129.84	129.55
	C2 I*BI	γ, δ'	129.84	129.80
	C2 IBI	δ', δ	129.84	129.80
	C2 BBB		129.84	129.85
	C2 BBI*		129.84	129.85
	C2 I*BB	γ	129.84	130.10
	C2 I*BI*	γ	129.84	130.10
	C2 IBB	δ	129.84	130.10
	C2 IBI*	δ	129.84	130.10
12	C2 BII	T, δ'_{T}	134.46	134.45
13	C2 BIB	T	134.70	134.70
	C2 BII*	T	134.70	134.70
	C2 III	T, δ'_{T}, δ_{T}	134.70	134.70
	C2 I*II	T, δ'_{T}, γ_{T}	134.70	134.80
14	C2 IIB	T, δ_{T}	134.94	134.95
	C2 III*	T, δ_{T}	134.94	134.95
	C2 I*IB	T, γ_{T}	134.94	135.05
	C2 I*II*	T, γ_{T}	134.94	135.05

Table VII
Observed and Calculated Chemical Shifts in BF Copolymer

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
	Saturated Carbons			
1	C4′ F		27.16	
2	C1 BB–		32.73	32.70
3	C1 BF–	Gγ'	32.93	32.90
4	C4 BFB	Q	35.75	35.80
5	C4 BFF	Q, Gδ_{Q}	35.85	35.95
	C4 FFB	Q, Gδ'_{Q}	35.85	35.95
6	C4 FFF	Q, Gδ_{Q}, Gδ'_{Q}	36.01	36.10
7	C1 FB–	Gα	46.19	46.20
8	C1 FF–	Gα, Gγ'	46.25	46.40
	Unsaturated Carbons			
9	C2 FF–	Gβ, Gβ'	122.42	122.40
10	C2 BF–	Gβ'	125.20	125.20
11	C2 FB–	Gβ	127.08	127.05
12	C2 BB–		129.86	129.85
13	C3 FB–	Gγ'	131.95	131.95
14	C3 BF–	Gα	140.31	140.30
15	C3 FFB	Gα, Gγ'	142.42	142.50
16	C3 FFF	Gα, Gγ'	142.50	142.50

The spectrum has 16 signals divided equally between the two zones of the spectrum (Table VII). Upfield we observe four groups of signals consisting of one signal around 27 ppm (*gem*-dimethyl group of F units, C4′-F), two signals centered at 32.8 ppm due to the butadiene carbons in the homopolymer dyads and to C1-F in BF– (signals 2 and 3, respectively), three signals centered at 35.8

Table VIII
Observed and Calculated Chemical Shifts in BT Copolymer

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
		Saturated Carbons		
1	C2′ T		16.29	
2	C4′ T		20.64	
3	C4 –TT	T, β_T, β'_T, $\delta_{T\beta}$, ($\delta'_{T\beta'}$)	30.70	30.70
4	C4 –BT	β, δ, ($\delta'_{T\beta'}$)	31.25	31.35
5	C1 BB–		32.70	32.70
	C4 –TB	T, β'_T	32.70	32.75
6	C1 BT–	α', $\gamma'_{\alpha'}$	39.74	39.75
7	C1 TB–	α, γ_α	40.70	40.60
8	C1 –TT	α, α'_α, $\gamma_{\alpha\alpha'}$, $\gamma'_{\alpha\alpha'}$	47.65	47.70
		Unsaturated Carbons		
9	C2 TBT	β, δ_β, δ'	128.56	128.60
10	C2 TBB	β, δ_β	128.87	128.90
11	C2 BBT	δ'	129.56	129.55
12	C2 BBB		129.85	129.85
13	C3 BBT	γ, ϵ_γ	130.05	130.10
14	C3 TBB	γ', $\epsilon'_{\gamma'}$	130.64	130.65
15	C3 TBT	γ, γ', ϵ_γ, $\epsilon'_{\gamma'}$	130.90	130.90
	C3 BTB	α, α'_α	130.90	130.90
16	C2 TTT	T, β_T, β'_T, $\delta_{T\beta}$, $\delta'_{T\beta'}$	131.42	131.45
	C3 BTT	α, α'_α, $\gamma_{\alpha\alpha'}$	131.42	131.45
17	C2 TTB	T, β_T, β'_T, $\delta_{T\beta}$	131.92	131.90
18	C3 TTB	α, α'_α, $\gamma'_{\alpha\alpha'}$, $\epsilon'_{\alpha'\gamma'}$	132.24	132.35
19	C2 BTT	T, β'_T, $\delta'_{T\beta'}$	132.43	132.45
20	C2 BTB	T, β'_T	132.89	132.90
	C3 TTT	α, α'_α, $\gamma_{\alpha\alpha'}$, $\gamma'_{\alpha\alpha'}$, $\epsilon'_{\alpha'\gamma'}$	132.89	132.90

ppm attributed to C4-F in the BFB triads (signal 4), the BFF and FFB triads (signal 5), and the FFF triads (signal 6), and finally two signals around 46.2 ppm assigned to C1-B in FB– (signal 7) and C1-F in FF– (signal 8). Of some interest is the value of the chemical shift of peak 7, far downfield, even though it is due to a carbon of the butadiene unit. This anomaly is connected with the strong deshielding effect of the *gem*-dimethyl group in the α position.

The presence of eight signals in the unsaturated zone instead of the seven expected on the basis of a sensitivity to the dyads (C2-B and C3-B in dyad BB are in fact equivalent by symmetry) requires a higher level of interpretation. In addition to the resonances of C2-F in the homopolymer dyad FF– (peak 9) and of the butadiene carbons in BB– (peak 12), the carbons C2-F in BF– (peak 10), C2-B in FB– (peak 11), C3-B in FB– (peak 13), and C3-F in BF– (peak 14) are clearly identified. The remaining peaks, peaks 15 and 16, which are very close together, are to be interpreted at the triad level; thus peak 15 corresponds to C3-F in FFB and peak 16 to C3-F in FFF.

Poly(butadiene-*co*-2-methylpentadiene). Two of the eight signals in the saturated region correspond to methyls C2′-T and C4′-T; the other six are interpretable at the dyad level. In fact seven resonances are forecast for the four dyads (C1-B and C4-B in BB coincide by symmetry), but one—C4-T in –TB—covers the resonance of the butadiene homopolymer (signal 5 at 32.70 ppm). This coincidence is due to accidental compensation of the effects of parameters T (+4.10 ppm) and β'_T (–4.05 ppm) (Table VIII).

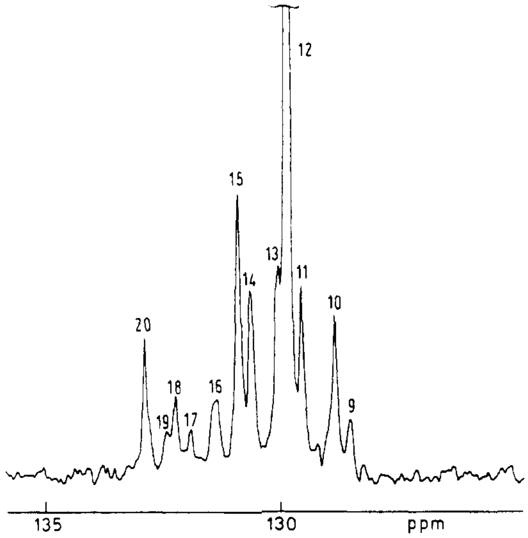

Figure 4. ^{13}C NMR spectrum of BT copolymer; unsaturated region in a sample containing 75% B units.

Table IX
Observed and Calculated Chemical Shifts in BD Copolymer

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
		Saturated Carbons		
1	C2′ D		18.00	
2	C2′ D		18.15	
3	C2′ D		18.31	
4	C1 DB–	β, γ_β	31.22	31.25
5	C1 BB–		32.70	32.70
6	C1 DD–	α', $\beta_{\alpha'}$, $\beta'_{\alpha'}$, $\gamma_{\alpha'\beta}$	33.37	33.30
7	C1 BD–	α', $\beta'_{\alpha'}$	34.81	34.90
		Unsaturated Carbons		
8	C2 BDD	T, α'_T, δ'_T	127.62	127.65
9	C2 BDB	T, α'_T	127.91	127.90
10	C2 DDD	T, α'_T, γ_T, δ'_T, $\delta_{T\gamma}$	128.17	128.25
11	C2 DDB	T, α'_T, γ_T, $\delta_{T\gamma}$	128.45	128.50
12	C2 BBD	δ'	129.50	129.55
13	C2 BBB		129.86	129.85
	C2 DBD	γ, δ', δ_γ	129.86	130.05
14	C2 DBB	γ, δ_γ	130.30	130.35

The unsaturated region offers 12 signals over a very narrow field (4 ppm) and is to be interpreted at the triad level. In the absence of inversions of the T units, there should be 15 signals, 7 of which are due to the B units and 8 to the T units. The 7 butadiene signals are all recognizable (peaks 9–15). In their turn the 8 T-unit signals form two partially superimposed quartets (Figure 4) attributed as follows: peaks 16, 17, 19, and 20 to C2-T and peaks 15, 16, 18, and 20 to C3-T. Attribution to single triads was achieved by comparison with computed values.

Poly(butadiene-*co*-2,3-dimethylbutadiene). The formation of this compound starting from the inclusion compound with PHTP reveals the extreme adaptability of the host structure to the dimensions of the guest molecule and shows how the principle of isomorphism or quasi-isomorphism, as a condition for inclusion copolymerization, is not applicable in the case of PHTP. Also from the structural and spectral points of view, BD copolymer is a very special case since both the the monomers are symmetric with respect to the direction of propagation of the chain. Thus only three dyads and six triads are distinguishable and at most four signals in the saturated region and eight in the unsaturated region can be observed.

In actual fact the spectrum presents 14 signals, 3 of which can be attributed to the methyls (the resonances of C2′-D and C3′-D in triad BDD give rise to a single signal) and 11 to the chain carbons (4 saturated and 7 unsaturated with accidental coincidence between the signals of triads BBB and DBD) (Table IX).

The relative narrowness of the spectral range (only 3.6 ppm for the CH_2 and 2.8 ppm for unsaturated carbons) has already been discussed in part 1, with reference to

Table X
Observed and Calculated Chemical Shifts in ID Copolymer

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
		Saturated Carbons		
1	C2′ I		16.05	
2	C2′ D		18.04	
3	C2′ D		18.13	
4	C4 –ID	β, β', γ_β	26.65	26.60
	C4 –II	β, β'	26.65	26.70
5	C4 –II*	β', $\gamma_{\beta'}$	28.26	28.25
6	C1 DD–	α', $\beta_{\alpha'}$, $\beta'_{\alpha'}$, $\gamma_{\alpha'\beta}$	33.30	33.30
7	C1 I*D–	α', $\beta_{\alpha'}$, $\beta'_{\alpha'}$	33.70	33.70
8	C1 ID–	α', $\beta'_{\alpha'}$, $\gamma_{\alpha'\beta'}$	34.78	34.90
9	C1 DI–	α', $\beta_{\alpha'}$, $\gamma_{\alpha'\beta}$	38.12	38.15
10	C1 I*I–	α', $\beta_{\alpha'}$	38.50	38.55
11	C1 II–	α', $\gamma_{\alpha'}$	39.70	39.70
		Unsaturated Carbons		
12	C3 –I–	α', (γ or δ)	123.9–124.2	$\simeq$124.0
13	C2 –D–	T, α'_{T}, (γ or δ)	127.9–128.3	$\simeq$128.0
14	C2 –I–	T, (γ or δ)	135.1	$\simeq$135.0

2,3-dimethylbutadiene homopolymer. The same principle explains the coincidence of the signals of triads BBB and DBD mentioned above.

Poly(isoprene-*co*-2,3-dimethylbutadiene). As already observed for BI copolymer, and as appears by comparison with BD copolymer, the presence of I units and of units deriving from a symmetric monomer simplifies the unsaturated region of the spectrum and makes the saturated region more detailed, mainly because of the chain inversions of the isoprene units.

Of the 14 signals observed, only three are in the low-field region and correspond simply to the three carbons C3-I (signal 12), C2-D (+C3-D) (signal 13), and C2-I (signal 14), with an ill-resolved fine structure which may be attributed to the effect of the copolymer sequences (Table X).

Three signals were assigned to the methyls: signal 1 to C2′-I, signal 2 to C2′-D in dyads ID and I*D (or, as an equivalent, to C3′-D in DI* and DI), and signal 3 to C2′-D (and C3′-D) in DD.

The eight remaining signals are attributed to the single dyads. In reality, nine signals are forecast for all possible dyads, the only overlapping being observed for C4-I in –ID and –II which correspond to peak 4. The values computed for these two signals are respectively 26.60 and 26.70 ppm, while the observed peak stands at 26.65 ppm. Better resolution conditions would very probably split its components.

Poly(pentadiene-*co*-isoprene). This copolymer, like TF copolymer, underwent a more detailed study. The spectrum consists of 35 signals, 2 of which belong to methyls C2′-I and C4′-P, 13 to the saturated carbons in the chain, and 20 to the olefinic carbons. Taking into consideration only the chain atoms, this copolymer presents the highest number of signals of all the copolymers examined by us, including TF copolymer itself (Figure 5). This complexity derives from the existence of monomer inversions, from the unsymmetrical nature of the monomers, and from the presence of a sufficient number of methyl substituents bonded to the chain (one for each monomer unit).

PI copolymer may be described as if it were generated by four pseudomonomers P, P*, I, and I* or as a succession of two units oriented freely in both directions, though not with equal probabilities. Ten dyads and thirty-two triads are thus expected, and a maximum of 16 signals for saturated chain carbons and of 64 signals for the unsaturated carbons.

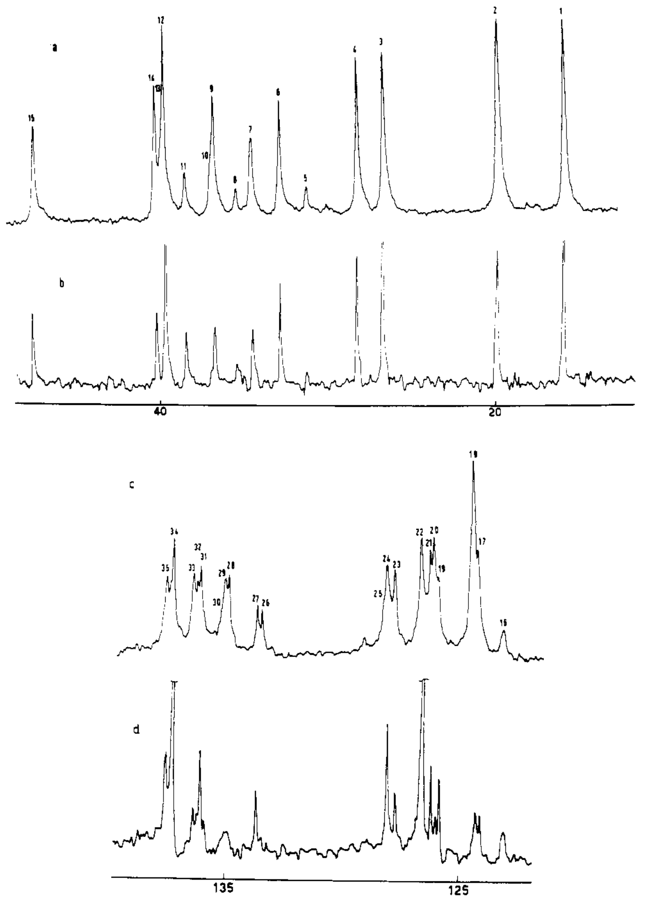

Figure 5. ^{13}C NMR spectrum of PI copolymer: (a) saturated carbons in a 42% P sample and (b) in a 20% P sample; (c) unsaturated carbons in a 42% P sample and (d) in a 71% P sample.

In the field from 26 to 48 ppm the resonance of all expected dyads can be recognized with the exception of C4-P in PP* (at 42.5 ppm no signal is detectable despite the low noise level). Two pairs of resonances have the same chemical shift: C4-I in –IP and in –II* (signal 4), and C1-P in P*P– and in IP– (signal 6).

An examination of the intensity of the single peaks in relation to the composition of the copolymer gives full agreement with the attribution give in Table XI. Signals 3, 9, 11, 12, and 14 belong to homopolymer sequences; the other saturated-carbon signals are more intense in the 50/50 copolymer and decrease symmetrically as the amount of either monomer is increased (copolymer dyad signals). Only signal 4 presents an anomalous pattern, being composed by two superimposed resonances, due to II* and IP dyads. The intensity pattern of signal 6 is typical of mixed dyads: this suggests the presence of only a slight contribution of P*P sequences to signal intensity, which is prevalently due to IP dyad.

Between 120 and 145 ppm we find 20 signals: 4 are homopolymeric, 12 have intensity variation typical of triads, and 4 more, generally weak and with complex intensity patterns, have chemical shift slightly dependent on composition. It seems clear that last signals are overlappings of resonances of infrequent sequences. By comparison with the computed chemical shifts it is possible to assign these signals to groups of triads containing units having inverted orientation (I* and P*).

As already stated, the triads formed by the four pseudomonomers can at most give rise to 64 signals, which is reduced to 56 if we eliminate all the triads containing the forbidden PP* sequences. If we take into account only the

Table XI
Observed and Calculated Chemical Shifts in PI Copolymer

signal no.	obsd carbon and sequence	parameters	exptl value	calcd value
Saturated Carbons				
1	C2′ -I-		16.01	
2	C4′ -P-		19.95	
3	C4 -II	β', β	26.72	26.70
4	C4 -IP	β', δ	28.26	28.15
	C4 -II*	$\beta', \gamma_{\beta'}$	28.26	28.25
5	C1 I*P-	β	31.28	31.25
6	C1 P*P-	γ', δ	32.85	32.70
	C1 IP-	γ', γ	32.85	32.80
7	C4 -PI	T, β_T	34.47	34.50
8	C4 -IP*	α, β'_α	35.48	35.50
9	C4 -PP	T, δ_T	36.81	36.80
10	C4 -PI*	T, γ_T	36.99	37.00
11	C1 I*I-	$\alpha', \beta_{\alpha'}$	38.50	38.50
12	C1 II-	$\alpha', \gamma_{\alpha'}$	39.75	39.70
13	C1 P*I-	$\alpha', \delta_{\alpha'}$	39.89	39.85
14	C1 PP-	α, γ'_α	40.28	40.30
15	C1 PI-	α, α'_α	47.71	47.70
Unsaturated Carbons				
16	C3 I[a]		122.90	
17	C3 IIP	α'	123.95	123.95
18	C3 III	$\alpha', \gamma_{\alpha'}$	124.16	124.15
19	C3 PIP	$\alpha', \gamma'_{\alpha'}$	125.66	125.65
20	C3 PII	$\alpha', \gamma_{\alpha'}, \gamma'_{\alpha'}$	125.83	125.85
21	C2 PPI	$\beta', \beta, \delta'_\beta$	126.00	126.10
22	C2 PPP	β', β	126.37	126.40
23	C2 IPI	$\beta', \delta, \delta'_\beta$	127.53	127.55
24	C2 P[a]		127.78	
25	C2 IPP	β', δ	127.93	127.85
26	C2 PII	T, β_T, δ'_T	133.31	133.25
27	C2 PIP	T, β_T	133.50	133.50
28	C2 III	T, δ_T, δ'_T	134.77	134.70
29	C2 IIP	T, δ_T	134.90	134.95
30	C2 I[a]		135.08	
31	C3 IPP	α	135.97	135.05
32	C3 P[a]		136.17	
33	C3 IPI	α, γ_α	136.29	136.40
34	C3 PPP	α, γ'_α	137.12	137.15
35	C3 PPI	$\alpha, \gamma_\alpha, \gamma'_\alpha$	137.43	137.50

[a] Sequences containing at least an inversion.

1–4 units (I and P and not I* and P*) the expected triad signals are reduced to 16, which is precisely the number of most abundant peaks found in the spectrum. Table XI gives their attributions.

A more complete analysis of PI copolymer, taking into account the probabilities of the single sequences will be presented as a part of the discussion of the mechanism of copolymerization in PHTP inclusion compounds.[2]

Conclusions

Our interpretation of the spectra of the ten copolymers and also of the six homopolymers discussed in part 1 is perfectly satisfactory both at a qualitative and at a quantitative level. No significant signal is ignored, and in many cases peaks have been recognized which only just emerge above background. In certain cases it might be worthwhile continuing the study at a stronger magnetic field, and in a few cases this was actually done; however, the basic framework of the interpretation did not change.[11]

A clarification would seem to be important with regard to the type and number of parameters used to compute the chemical shift (Table II in part 1). It might be objected that the numerous distinctions between parameters of the same type (e.g., γ, γ_T, γ_α, γ_β, $\gamma_{\alpha'}$, $\gamma_{\beta'}$) makes our scheme more descriptive than predictive. This choice, however, was aimed to optimizing the accuracy of the computed value, given the dense crowding often observed in the spectra. It should in any case be borne in mind that attribution of signals was in most cases based on logical rather than numerical criteria.

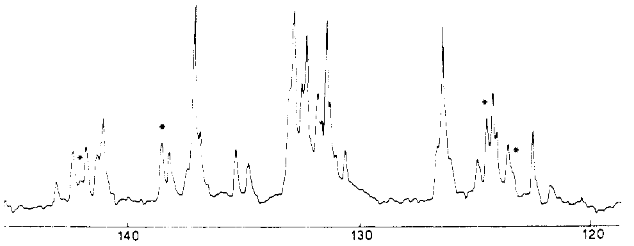

Figure 6. ^{13}C NMR spectrum of PTF terpolymer (P:T:F ratio: 0.3:0.5:0.2); unsaturated region. Asterisks mark detectable terpolymeric triads.

Nonetheless, to demonstrate the predictive value of the computation scheme employed, we report in Figure 6 the spectrum of the terpolymer obtained in PHTP from pentadiene, 2-methylpentadiene, and 4-methylpentadiene (PTF terpolymer). The terpolymer spectrum can for the most part be interpreted on the basis of the known spectra of the three PT, PF, and TF copolymers. However, there exist six mixed triads giving rise to 12 signals in the unsaturated zone, whose chemical shifts are exactly predicted. Eight of them coincide with known copolymer signals, two are clearly observed in the spectrum and are attributed to C2-P and C3-P in the FPT triad (exptl 124.42 and 138.53 ppm; calcd 124.45 and 138.60 ppm), and the remaining two, attributed to C2-F and C3-F in the PFT triad (exptl 123.30 and 142.08 ppm; calcd 123.30 and 141.90 ppm), are detected as apparent shoulders (Figure 6).

A future publication will deal with the various features and limits of copolymerization in PHTP.[2] Nonetheless it is worthwhile anticipating here a suggestion deriving from a comparative examination of the structure of the homopolymers and copolymers containing units having inverted orientation (I*, P*, etc.). In addition to the topochemical rule already put forward[1] (absence of substituents in terminal position), the direction of insertion may also be governed by an electronic factor, in particular by the relative stability and reactivity of the substituted allyl radicals responsible for polymerization.

Acknowledgment. Our thanks are due to Gammatom, Guanzate, Como, Italy, for use of the γ ^{60}Co source. The research was financed by contributions of Consiglio Nazionale delle Ricerche, Rome, Italy, and by Ministero della Pubblica Istruzione, Rome, Italy.

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