^{13}C NMR Spectra of Methyl-Substituted 1,4-*trans*-Polybutadienes. 1. Method of Assignment and Spectra of Some Homopolymers

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ABSTRACT: The availability of a wide series of homo- and copolymers of methyl-substituted butadienes, all having a 1,4-trans structure and obtained by inclusion polymerization in perhydrotriphenylene, has made it possible to carry out a systematic study of their ^{13}C NMR spectra. A scheme is proposed to predict the chemical shift of the saturated and unsaturated carbons of the main chain. The spectra of the following polymers are compared and discussed: 1,4-*trans*-polybutadiene, isotactic 1,4-*trans*-polypentadiene, 1,4-*trans*-polyisoprene, 1,4-*trans*-poly(4-methylpentadiene), isotactic 1,4-*trans*-poly(2-methylpentadiene), and 1,4-*trans*-poly(2,3-dimethylbutadiene).

Inclusion polymerization of vinyl and diene monomers is a well-established method of producing polymers having a defined structure.[1-8] In particular, the polymers of numerous diene monomers obtained by inclusion polymerization in perhydrotriphenylene (PHTP) all have a very pure 1,4-trans structure. Many of these compounds are crystalline and some have a high degree of isotacticity.[3,4,6,9,10] By operating under suitable conditions it has been found possible to obtain optically active polymers[11,12] and also polymers with extended-chain morphology.[13]

More recently, two major steps forward have been made in this field: the extension of this method to the production of random copolymers, and the ever more extensive application of ^{13}C NMR spectroscopy to the determination of the microstructure of macromolecular compounds, both with regard to the sequences of various monomer units in the copolymers and with regard to steric sequences in homopolymers.

In this series of papers we intend to examine the ^{13}C NMR spectra of diene homo- and copolymers obtained by inclusion polymerization in PHTP. Our aim is twofold: to determine the constitutional and steric microstructure of the products and to establish a general method of interpreting the ^{13}C NMR spectra of diene polymers having 1,4-trans structure, containing a variable number of methyl groups in different positions. A forthcoming article[14] will be dedicated to the peculiar features of inclusion copolymerization, to the criteria for selecting pairs of monomers that can be used with a given host, and to the conditions in which the reaction can be achieved.

General Remarks

Our earlier studies on inclusion polymerization in PHTP had shown that this process, in addition to a high degree of constitutional and stereochemical control, has only a very limited selectivity in relation to the shape and dimensions of the monomers, much less than that observed with urea and thiourea. As a result of the greater adaptability, our procedure makes it possible to obtain a wide variety of macromolecular compounds, all having the same well-defined basic structure. As a whole, the findings obtained by various techniques (IR, X-ray, and preliminary studies by ^{1}H and ^{13}C NMR), together with considerations of reactivity, provide a highly consistent and homogeneous picture of the nature of the polymers, which can be used as a guideline to interpret the ^{13}C NMR spectra in the more complex cases.

As regards the homopolymerization of conjugated dienes, this picture can be outlined as follows:

(1) All the monomer units have 1,4-trans structure (no findings suggest the presence of 1,4-cis and 1,2 units or of cyclic structures).

(2) With the sole and noteworthy exception of polyisoprene, all the polymers have only head-to-tail sequences.

(3) When stereoisomerism is possible around tetrahedral carbon atoms, the isotactic structure is far more commonly preferred.

The first point can easily be explained in terms of the principles of least motion[15] and of topochemical control[16] if we assume that in the included state the monomer has an anti conformation around the central simple bond of the conjugated system.

The absence of head-to-head sequences has been attributed to the excessive distance supposed to exist between the reactive atoms of two adjacent monomers when these have trans methyl groups facing each other.[10] It follows that only nonsubstituted monomers, or monomers substituted in an internal position (e.g., butadiene, 2,3-dimethylbutadiene, and isoprene) might be inserted in the two opposite orientations 1–4 and 4–1, but sometimes the two possibilities are equivalent by symmetry and hence the phenomenon cannot be observed.

With reference to point 3, the degree of isotacticity was found to be so high that in most cases the interpretation of spectra may ignore complications due to the presence of different steric sequences.

We wish to stress that all the signals in the spectra can be attributed to the polymer structure. In very few cases three small signals due to PHTP residues have been observed at 26.60, 30.17, and 47.16 ppm, but this impurity is easily removed with a suitable solvent (acetone). A different problem could arise from the presence of PHTP fragments bonded to the polymer and derived from starting or quenching radicals. In a previous paper,[9] we demonstrated by using ^{14}C-labeled PHTP that the number of PHTP radicals bonded to the chain varies, depending on the conditions, from 0.3 to 1. In view of the high molecular weight of our polymers (>100 000) the influence of such end groups in the spectrum is negligible.

The extension of observations 1–3 to copolymers cannot be taken for granted. Copolymerization is a process having a greater number of degrees of freedom with respect to homopolymerization, and as a consequence irregularities in concatenation and configuration are possible. This might well be even more significant in solid-state copolymerization, in which the disturbance due to the presence of different monomers might lead to considerable local modifications in the crystal structure. A second

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Table I
Nomenclature of Diene Homopolymers and Copolymers[a]

monomer	symbol	numbering of carbon atoms
butadiene	B	$-CH_2CH{=}CHCH_2-$ 1 2 3 4
pentadiene	P	$-CH_2CH{=}CHCH(CH_3)-$ 1 2 3 4 4′
isoprene	I	$-CH_2C(CH_3){=}CHCH_2-$ 1 2 2′ 3 4
4-methylpentadiene	F	$-CH_2CH{=}CHC(CH_3)_2-$ 1 2 3 4 4′,4″
2-methylpentadiene	T	$-CH_2C(CH_3){=}CHCH(CH_3)-$ 1 2 2′ 3 4 4′
2,3-dimethylbutadiene	D	$-CH_2C(CH_3){=}C(CH_3)CH_2-$ 1 2 2′ 3 3′ 4

[a] Homopolymers will be indicated as poly-B, poly-I, etc; copolymers as BI copolymer, BP copolymer, etc.

reason for caution involves the fact that certain limiting conditions mentioned above are no longer applicable. With particular reference to point 2, if our interpretation is correct, the insertion of nonterminally substituted monomers such as butadiene should remove the steric interactions inhibiting inversion of orientation.

So long as these observations are taken into account, the selection rules given above are perfectly adequate to describe copolymers obtained in PHTP inclusion compounds.

Table I gives symbols and numbering used in the discussion that follows. The chemical shift of a given carbon depends not only on the nature of the monomer unit in which it is inserted (n unit) but also on the nature of the units immediately preceding ($n - 1$) and following it ($n + 1$). Each triad of monomer units is denoted by a triplet of letters, generically expressed as XYX. Some signals, especially those of saturated carbons, are in reality sensitive only to sequences of two monomer units. It must be borne in mind that dyads XY and YX are not equivalent, as they are in vinyl polymers. Furthermore carbons C1 and C4 (or C2 and C3) of every monomer unit generally have a different chemical shift; as a result, the spectrum of the main-chain carbons should present up to eight signals at the dyad level (and up to 16 at the triad level). To facilitate identification of the sequences in question we have in this context considered the dyads as partially degenerate triads, indicating them as -YX (dyad common to triads XYX and YYX), XY- (dyad common to triads XYX and XYY), etc.

Spectral analysis was carried out in various stages. The first level consisted in identifying (where necessary) the degree of substitution of the carbon atom under consideration (CH_3, CH_2, CH, and quaternary C) obtained by normal spectroscopic techniques. After this, the homopolymer sequences were recognized and then the copolymer sequences with different content of the two components. Lastly, copolymer sequences having the same composition but different arrangement of monomer units were examined and recognized. The chemical shift of the homopolymer triads in the copolymers was found to be equal to that of the corresponding signal in the homopolymer. In cases in which solubility problems make it impossible to obtain the spectrum of the homopolymer under normal conditions (room temperature, $CDCl_3$ as solvent), samples of polymer containing small quantities of comonomer (2–5%) were prepared; these provided adequate solubility with practically no effect on the spectrum.

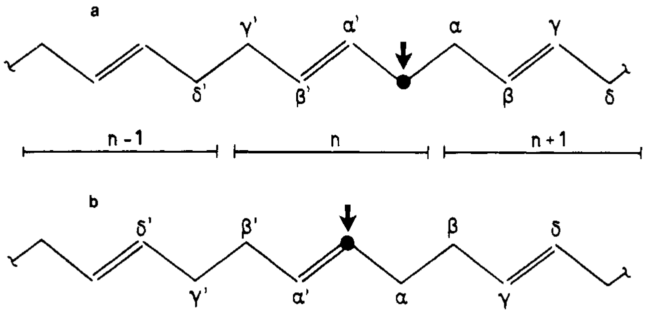


Figure 1. Position of the substituents along the chain referred to saturated (a) and unsaturated (b) carbons.

The comonomer ratio of the triad at which each signal is sensitive has been obtained by means of simple intensity criteria: this method is particularly useful when groups of signals that center on the same carbon are considered, because the assumption of a Bernoulli distribution is no longer necessary. In the case of partially degenerate triads (e.g., -XY) the intensity dependence on comonomer composition is the same as that of the corresponding dyads.

A New Set of Parameters

The intensity considerations described in the preceding section make it possible to assign more than half of the signals observed in the spectrum. For a complete analysis it is necessary to establish criteria capable of distinguishing triads of equal composition and different distribution, such as XXY and YXX. For this purpose we used a set of additive parameters applicable to the macromolecular skeleton common to all the polymers we investigated. This method is similar to those already in use for the computation of the chemical shift of the ^{13}C NMR spectra of various classes of compounds, the sole differences consisting in the choice of the reference molecule and in the definition of the parameters.[17,18] The diene homo- and copolymers obtained by inclusion polymerization in PHTP can be considered as 1,4-*trans*-polybutadienes perturbed by the presence of methyl groups (up to two for each monomer unit). Hence the structure of 1,4-*trans*-polybutadiene was chosen as a reference in this study. It has two nonequivalent carbon atoms, one saturated and one unsaturated, to which are applied two different groups of parameters related to the presence of methyl groups on the same carbon and on its neighbors. The symbols α, β, γ, δ, and ϵ denote the various chain positions in which a substituent may be located (Figure 1). The same letters marked with a prime (α', β', γ', δ', and ϵ') indicate the opposite chain direction, the convention being to consider α the saturated atom and α' the unsaturated atom adjacent to the atom being considered. The two parameters Q and T are used when the atom being considered is quaternary or tertiary. The letter G before the Greek letter indicates that there are two geminal methyls in that position. The chemical shift could be calculated in the following way (in ppm from $(CH_3)_4Si$):

$$\nu = \text{constant term} + \text{Q (or T)} + \alpha + \alpha' + \beta + \beta' + \ldots \text{(+corrective terms)}$$

We found it preferable to suppress the corrective terms due to interaction between substituents and to incorporate them in the parameter values, which are differentiated from each other and marked by a suitable subscript (Table II). The effect of interaction was attributed to the parameters relating to the more distant substituents according to the following hierarchy: α closer than α' than

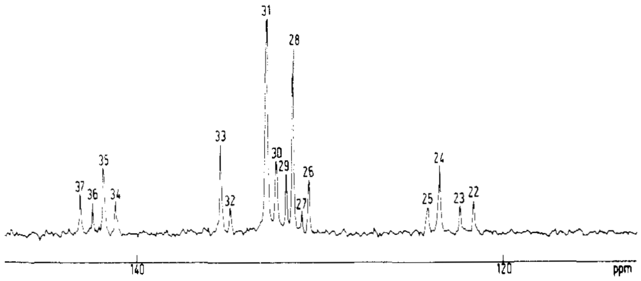


Figure 2. ^{13}C NMR spectrum of the unsaturated region of a TF copolymer containing 73% T units.

Table II
Parameter Set for Carbon-13 Chemical Shift of Methyl-Substituted 1,4-*trans*-Polybutadienes

symbol	value	no. of direct readings	no. of occurrences
Saturated Carbons (Constant Term = 32.70)			
Q	3.10	1	8
T	4.10	1	14
α	7.60	2	12
Gα	13.50	2	6
α'	7.00	1	17
α'_{α}	7.40		6
β	−1.45	2	9
β_Q	0.50		2
β_T	−2.30	1	5
$\beta_{\alpha'}$	−1.20	1	6
β'	−4.55	3	8
β'_T	−4.05		7
β'_{α}	−4.80	1	1
$\beta'_{\alpha'}$	−4.85	2	4
γ	0.10	1	1
γ_T	0.20	1	1
γ_{α}	0.30	1	7
$\gamma_{\alpha'} = \gamma_{\alpha\alpha'} = \gamma_{\alpha'\beta'}$	$\simeq$0		4
$\gamma_{\alpha'\beta}$	−0.40	2	3
$\gamma_{\beta} = \gamma_{\beta\beta'}$	−0.10	1	3
$\gamma_{\beta'}$	0.10	1	2
γ'	$\simeq$0		6
$\gamma'_{\alpha} = \gamma'_{\alpha'} = \gamma'_{\alpha\alpha'}$	$\simeq$0		8
Gγ'	0.20	2	6
$\delta = \delta_Q = \delta_T$	$\simeq$0		7
$\delta_{\alpha'} = \delta_{Q\beta} = \delta_{T\beta}$	0.15		7
Gδ_Q	0.15	2	4
Gδ_T	0.15		2
G$\delta_{T\beta}$	0.30		1
$\delta' = \delta'_Q = \delta'_T$	$\simeq$0		8
$\delta'_{T\beta'}$ = Gδ'_Q = Gδ'_T	0.15	2	11
G$\delta'_{T\beta}$ = G$\delta'_{T\beta'}$	0.30		2
Unsaturated Carbons (Constant Term = 129.85)			
T	4.85	1	29
α	6.20	2	25
Gα	10.45	2	8
α'	−5.90	1	7
α'_T	−6.80		6
α'_{α}	−5.15		12
$\beta = \beta_{\alpha} = \beta_T$	−1.20	2	22
Gβ	−2.80	2	6
Gβ_T	−1.85		4
β'	−2.25	2	13
β'_T	−1.80		12
Gβ'	−4.65	2	6
γ	0.25	2	7
$\gamma_{\alpha} = \gamma_T$	0.35	4	10
$\gamma_{G\alpha}$	0.65	2	2
$\gamma_{\alpha\alpha'}$	0.55	6	6
$\gamma_{\alpha'}$	0.20	2	2
γ'	1.05	2	12
γ'_{α}	1.10	2	2
$\gamma'_{G\alpha}$	0.95		2
$\gamma'_{\alpha'} = \gamma'_{\alpha\alpha'}$	1.70	2	10
Gγ'	2.10	2	2
Gγ'_{α}	2.20		4
G$\gamma'_{\alpha'}$	3.95		2
$\delta = \delta_T = \delta_{\beta} = \delta_{\gamma}$	0.25	3	25
$\delta_{T\beta}$	0.20	2	6
δ'	−0.30	4	7
δ'_T	−0.25	7	9
$\delta'_{\alpha'}$	−0.25		2
$\delta'_{\beta'}$	−0.35	4	4
$\delta'_{T\beta'}$	−0.45	6	6
$\delta'_{G\beta'}$	−0.70	2	2
$\epsilon'_{\gamma'}$	−0.25		2
$\epsilon'_{\alpha\gamma'} = \epsilon'_{\alpha'\gamma'}$	−0.25	4	8

β, β', and so on. As an example the parameter $\delta_{T\beta}$ refers to the influence of the starred methyl on the chemical shift of the italicized carbon (which is a tertiary carbon and is influenced by a β methyl) in the sequence

$$-\mathrm{CH_2CH{=}CH}\mathit{CH}\mathrm{(CH_3)CH_2C(CH_3){=}CHCH(CH_3)^*} -$$

or in the sequence

$$-\mathrm{CH_2CH_2CH{=}}\mathit{C}\mathrm{(CH_3)CH_2CH(CH_3)CH{=}C(CH_3)^*} -$$

according to whether it refers to a saturated or unsaturated carbon. Differentiation between parameters was introduced when requested by at least one experimental evidence.

The constant terms were obtained directly from the spectrum of polybutadiene. The chemical shift of each signal was expressed as the sum of contributions due to the substituents up to a distance of five bonds in the chain. The chemical shifts of signals presenting the same set of parameters in different polymers were compared in order to ascertain the validity of the experimental finding. In all cases differences in chemical shifts were found to be less than 0.1 ppm (usually 0.05).

Comparison between situations differing by a single parameter in the same spectrum makes it possible to determine the value of the parameter directly. When a single parameter was measured in different points of the spectrum or in different spectra, deviation from the mean value was always found to be below ±0.1 ppm. The mean value was rounded off to 0.05 ppm. Only a limited number of parameters were obtained indirectly by subtracting from the experimental datum the value calculated for the parameters already known. This involves more considerable error in determining the parameter. The number of direct readings of each parameter is indicated in Table II, together with the total number of occurrences.

In some instances, two attributions for a given signal can be interchanged, which leads to two distinct sets of solutions for the values of the parameters involved. In such cases we chose the one which is consistent with analogous parameters determined in an independent way. In this context we illustrate the assignment of the signals of the copolymer obtained from 2-methylpentadiene and 4-methylpentadiene (FT copolymer) at low field (Figure 2). In this region the spectrum presents 16 signals (from 22 to 37) divided into 4 quartets, in agreement with a sensitivity toward triads of monomer units. Multiplicity analysis and comparison with the spectra of the homopolymers have made it possible to assign signals 22–25 to carbon 2 in 4-methylpentadiene (C2-F), signals 26–29 to C2-T, signals 30–33 to C3-T, and signals 34–37 to C3-F. In the first quartet the homopolymer signal FFF (corresponding to signal 23) and that of the alternate triad TFT (signal 24) were attributed on the basis of intensity, while signals 22 and 25 might be due to sequences FFT and TFF or vice versa. As indicated in Table III, the first attribution leads to reasonable values of parameter $\delta'_{G\beta'}$ (−0.70, to be compared with the value of −0.40 found for δ'). If this assignment were inverted, the parameter would be found to have a value of +1.75, which would be totally unjustified. In the same way, sequence TFF is assigned to signal 25;

Table III
Partial Analysis of the Unsaturated Region of the TF Copolymer (C2·F Carbon)[a]

sequence	parameters	no. of resonance and chem shift		value of parameters	
				δ_β	$\delta'_{G\beta'}$
FFT	$G\beta + G\beta' + \delta'_{G\beta'}$	*22*	*121.70*		*−0.72*
		25	124.16		*+1.74*
FFF	$G\beta + G\beta'$	*23*	*122.42*		
TFT	$\beta + G\beta' + \delta_\beta + \delta'_{G\beta'}$	*24*	*123.47*		
TFF	$\beta + G\beta' + \delta_\beta$	*25*	*124.16*	*+0.20*	*−0.69*
		22	121.70	−2.26	+1.77

[a] Correct assignments and parameter values are italicized.

Table IV
^{13}C NMR Spectra of Various Polybutadiene Samples

sample	C1	C2
low-molecular-weight homopolymer	32.78	129.91
butadiene–2,3-dimethylbutadiene copolymer	32.70	129.87
butadiene–2-methylpentadiene copolymer	32.72	129.86
butadiene–4-methylpentadiene copolymer	32.71	129.86
butadiene–3-methylpentadiene copolymer	32.70	129.84
average values	32.72	129.87
rounded values	32.70	129.85

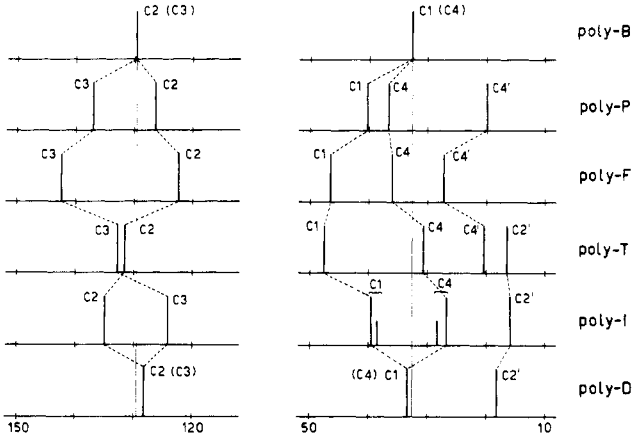


Figure 3. Comparative view of the ^{13}C NMR spectra of the homopolymers.

the new reading of $\delta'_{G\beta'}$ corresponds to the previous one. An independent test for this attribution is given by δ_β which is found to be equal to 0.20, in agreement with the other δ values.

An examination of Figure 1 and Table II allows us to explain the differing sensitivities of the signals of saturated and unsaturated carbon atoms as regards the length of the copolymer sequences. As a matter of fact the high-field part of the spectrum may in many cases be interpreted in terms of dyads and also presents many unresolved signals. On the other hand, the low-field region more frequently shows complete resolution at the triad level. The influence of the structure of the $n - 1$ unit on carbon C4 of the n unit (or of that of the $n + 1$ unit on carbon C1) implies at most a δ' effect, which often is equal to zero or in any case is very small. In their turn, the unsaturated carbons are sensitive to the triad composition through the presence of substituents in β and γ' or in γ and δ'. In both cases the corresponding parameters are not negligible and significant splittings of signals are observed.

An analogous set of parameters for the methyl signals is not required because of their limited sensitivity to the microstructural environment. When a detailed pattern of signals is observed, as in the spectrum of the TF copolymer (mentioned above), assignment was made by taking into account the substituent effect as discussed above, although not expressed in numeric form.

Results and Discussion

Polybutadiene. Because of its insolubility it is impossible to record the spectrum at room temperature of samples of 1,4-*trans*-polybutadiene (poly-B) prepared according to the usual techniques. By using high radiation dose and a short postpolymerization time we nonetheless succeeded in obtaining a sample with a rather low molecular weight which was sufficiently soluble. Its spectrum consists of only two signals (Figure 3).

A second method to obtain a soluble polymer consists in copolymerizing butadiene with small quantities of a diene comonomer. Results are given in Table IV. Comparison of our findings with those reported by Priola et al.[19] (32.80 and 130.1 ppm for *trans*-poly-B and 27.40 and 129.7 ppm for *cis*-poly-B) further confirms the trans structure already assigned to our polymer on the basis of IR and X-ray spectra and of its thermal behavior (solid–solid endothermal transition at 55–65 °C and melting at 120–130 °C).[20] The mean values of the chemical shift obtained from the various samples examined were used as constant terms in our system of parameters.

Polypentadiene. The spectrum of the polymer obtained from *trans*-1,3-pentadiene included in PHTP had already been partially discussed by Zetta, Gatti, and Audisio[21] in connection with the spectrum of the polymer obtained from *cis*-1,3-pentadiene included in deoxycholic acid (DCA). The polymer obtained in PHTP is highly stereoregular: its ^{13}C NMR spectrum shows five very sharp signals, which correspond to those observed in a sample of isotactic 1,4-*trans*-poly-P obtained by coordination polymerization[22] (Table V), while the polymer obtained in DCA has a fine structure linked to the presence of irregular steric sequences. The same conclusion had been reached on examining the saturated polymer obtained from the preceding one by reaction with diimide (this polymer corresponds to an alternate isotactic ethylene–propylene copolymer). The spectrum of our polymer shows no traces of h–h or t–t sequences, the signals of which could be expected to be located around 42.5, 33.0, and 18.5 ppm.[23]

Polymerization of *cis*-1,3-pentadiene included in PHTP also gives rise to a head-to-tail 1,4-trans polymer that is predominantly isotactic. It produces five signals coinciding with those obtained from the trans monomer. The signal of unsaturated carbon C2 shows a considerable asymmetric broadening, not resolved at 25.2 MHz but clearly split into two other weak signals at 50.3 MHz. Copolymerization of mixtures of *cis*- and *trans*-1,3-pentadiene having differing stereoisomeric contents has shown that the extent of this irregularity is connected with the quantity of cis monomer and is undoubtedly of steric origin.

Polyisoprene. Polyisoprene obtained in PHTP poses certain structural problems which can be resolved with clarity only by means of ^{13}C NMR spectroscopy. The trans configuration of the trisubstituted double bond is supported only by relatively weak evidence in the IR spectrum.[3,10] However a highly regular 1,4-trans structure is

Table V
^{13}C NMR Spectra of Substituted 1,4-*trans*-Polybutadienes[a]

monomer		methyl carbons		saturated carbons		unsaturated carbons	
		C2′	C4′	C1	C4	C2	C3
pentadiene	exptl		19.94	40.29	36.81	126.42	137.23
	calcd		nd	40.35	36.80	126.40	137.10
isoprene	exptl	15.99		38.49-*39.72*	*26.72*-28.26	134.80	124.17
	calcd	nd		38.55-39.70	26.70-28.25	134.80	124.10
4-methylpentadiene	exptl		27.24	46.42	36.05	122.36	142.46
	calcd		nd	46.40	36.10	122.40	142.40
2-methylpentadiene	exptl	16.31	20.30	47.65	30.75	131.44	132.85
	calcd	nd	nd	47.65	30.75	131.45	132.90
2,3-dimethylbutadiene	exptl	18.15		33.32		128.21	
	calcd	nd		33.35		128.30	

[a] Italicized values correspond to h-t sequences.

not substantiated by X-ray analysis: moreover, DSC curves show a weak endothermal transition around room temperature, while the melting point of pure 1,4-*trans*-poly-I, of both synthetic and natural origin, is above 65 °C.[24] Nothing was known as to the nature of the structural irregularities that inhibit crystallinity in our polymer.

The ^{13}C NMR spectrum of poly-I obtained by inclusion polymerization in PHTP presents seven signals: one attributed to the C2′ methyl, two to the unsaturated carbons C2 and C3, and the other four (intensities 85:15:15:85) to the saturated carbons C1 and C4 situated in different structural environments. The presence of 1,2 or 3,4 units can be excluded because of the absence of the corresponding signals in the unsaturated region. Its trans structure is confirmed by comparison with findings in the literature: the chemical shifts of C2′ and C1 (see Table V) agree with those reported in the literature for 1,4-*trans*-poly-I (15.87 and 39.67 ppm) and not with those of 1,4-*cis*-poly-I (23.25 and 32.25 ppm).[25,26]

As already reported in a preliminary communication,[12] the minor components in the saturated-carbon spectrum are due to the presence of monomer units inserted in the opposite way, giving rise to head-to-head:tail-to-tail sequences. In particular, the h–h sequence involves carbon C1 and the t–t sequence carbon C4. The spacing between the two components of each doublet is not equal ($|\Delta\nu(\mathrm{C1})| = 1.24$, $|\Delta\nu(\mathrm{C4})| = 1.54$), which would appear to violate the additivity rules on which our interpretation is based. As a first approximation the chemical shift of the carbon atoms under consideration would be expressed by

$$\mathrm{C1(h{-}t)} = \alpha' + \gamma; \qquad \mathrm{C1(h{-}h)} = \alpha' + \beta$$

$$\mathrm{C4(h{-}t)} = \beta + \beta'; \qquad \mathrm{C4(t{-}t)} = \beta' + \gamma$$

whence

$$|\Delta\nu(\mathrm{C1})| = |\Delta\nu(\mathrm{C4})| = |\beta - \gamma| = 1.55$$

If, however, we take into account the interactions between substituents, the signals parameterize as follows:

$$\mathrm{C1(h{-}t)} = \alpha' + \gamma_{\alpha'}; \qquad \mathrm{C1(h{-}h)} = \alpha' + \beta_{\alpha'}$$

$$\mathrm{C4(h{-}t)} = \beta + \beta'_{\beta}; \qquad \mathrm{C4(t{-}t)} = \beta' + \gamma_{\beta'}$$

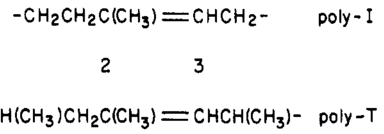
As a result, $|\Delta\nu(\mathrm{C1})|$ is no longer necessarily equal to $|\Delta\nu(\mathrm{C4})|$. The physical basis of this interpretation involves the different conformational equilibrium around the single bonds of the segment =C–C–C–C= when only one or both or neither unsaturated carbon atom is bound to a methyl substituent. Numerically (Table II) $\beta_{\alpha'}$ differs from β, while the other parameters do not require any correction, since the methyl groups are far enough from each other to be actually independent.

Further confirmation comes from comparison with the spectrum of squalene, an acyclic triterpene consisting of 1,4-trans head-to-tail and tail-to-tail isoprene sequences:

$$(\mathrm{CH_3C(CH_3){=}CHCH_2CH_2C(CH_3){=}CHCH_2CH_2C(CH_3){=}CHCH_2})_2$$

According to Roberts,[27] the signals at 27.2, 40.2, and 28.7 ppm correspond to carbons C8, C9, and C12, which in our notation are indicated as h-t C4, h-t C1, and t-t C4, respectively.

The attribution of the two unsaturated signals C2 and C3 of poly-I is deduced from a study of the off-resonance decoupled spectrum.[25,27] Alternatively, and as an example of attribution based on qualitative considerations of the effect of the substituents, the same attribution is obtained by comparison of the spectrum of poly-I with that of head-to-tail poly(2-methylpentadiene) (poly-T). This polymer gives olefinic signals very close to each other, in a position intermediate between the two signals of polyisoprene (Table V and Figure 3). The structures of the two polymers



$$-\mathrm{CH_2CH_2C(CH_3){=}CHCH_2}- \quad \text{poly-I}$$

$$-\mathrm{CH(CH_3)CH_2\overset{2}{C}(CH_3){=}\overset{3}{C}HCH(CH_3)}- \quad \text{poly-T}$$

differ insofar as the latter has two additional methyls in positions β and β' with respect to C2 and in positions α and γ' with respect to C3. All parameters β and β' being known to be negative, while α is highly positive (and γ relatively small), the C2 signal in polyisoprene cannot be other than the low-field signal. This interpretation is independent of the assignment of atoms C2 and C3 in poly-T. The spectrum recorded at 25.2 MHz shows weak poorly resolved signals at 134.95 and 135.15 ppm at the side of the signal from unsaturated carbon C2, due to the different distribution of the h-t, h-h, and t-t sequences in the polymer. A detailed study of this problem, using a higher field spectrometer, is now being carried out.[28]

Poly(4-methylpentadiene). This polymer yields a five-signal spectrum, the attribution of which is self-evident. Because of the presence of *gem*-dimethyl groups in α, γ, etc., most of the signals are shifted downfield with respect to polypentadiene (Table V and Figure 3). Exceptions are C4 (which becomes a quaternary carbon) and C2, which undergoes the shielding effect of the two *gem*-dimethyl groups in positions β and β'.

It should be noted that the effect of the *gem*-dimethyl group is not double that of a single methyl in the same position, as had already been observed for the copolymer butadiene–isobutene[19] and for hydrogenated poly(4-methylpentadiene).[29] It must also be borne in mind that parameters Gα, Gβ, etc. refer to the entire *gem*-dimethyl group and not to the single methyls.

Poly(2-methylpentadiene). This crystalline, high-melting polymer is of very low solubility at room temperature; its spectrum has been deduced from those of copolymers having a low comonomer content, in a manner similar to that already described for polybutadiene. It was assumed to have an isotactic structure.[10] This hypothesis has recently been confirmed definitively by examining the saturated polymer obtained by reduction with diimide.

This reaction converted the poly-T into hemiisotactic polypropylene, a head-to-tail polymer consisting of an alternation of tertiary atoms with a definite configuration and of tertiary atoms with a random configuration.[30,31] Supposing the unsaturated polymer to have 100% isotacticity, some peaks in the methyl spectrum of polypropylene (those corresponding to the pentads mrmr, mrmm, and rmrr) are expected to disappear completely. Statistical analysis of the saturated polymer, together with an evaluation of the residual intensity of the forbidden signals made it possible to ascertain that the degree of isotacticity of poly-T, expressed in terms of isotactic dyads, is above 96%.[31] As a matter of fact, the spectrum of the unsaturated polymer presents very sharp signals, and even when it is recorded under conditions of highest resolution there is no trace of a fine structure due to the presence of various stereosequences.

The assignment of the two low-field resonances to the unsaturated carbons C2 and C3 was obtained by examination of the off-resonance decoupled spectrum.

As regards the methyl signals, it is interesting to notice the limited dependence of their chemical shift on the presence of nonadjacent methyl groups in the same monomer unit, observed in the entire series of polymers examined in this study: signals C2′ and C4′ of poly-T are separated by only 0.3–0.4 ppm from those of polyisoprene and of polypentadiene. The influence of the substituents present in the neighboring monomer units is negligible in most cases. The only exception was found for the influence of a *gem*-dimethyl group in the $n - 1$ unit, as observed in the TF copolymer.

Miyata and Takemoto have recently reported the ^{13}C NMR spectrum of poly-T obtained from the cis monomer included in deoxycholic acid.[32] Their data (16, 31, 48, 132, and 133 ppm) are in qualitative agreement with those given in Table V.

Poly(2,3-dimethylbutadiene). In the first article on inclusion polymerization in PHTP the structure of this polymer had been indicated as 1,4-trans on the basis of the IR and X-ray spectra.[3] The melting point (265 °C) also agrees with that of the 1,4-trans polymer[24] and with that observed by Brown and White for the polymer obtained in thiourea.[1] Direct determination of the structure of this last-mentioned polymer was later achieved by Chatani and Nakatani.[33]

As regards its ^{13}C NMR spectrum, difficulties of attribution are due to two facts: the very limited solubility of the polymer and the almost identical local structures of the trans and cis polymers. This means we may expect only small differences in the positions of the signals of the two stereoisomers. Cantow et al. have extrapolated the spectrum of the trans isomer from that of soluble polymers containing variable quantities of trans and cis monomer units.[34] As regards the high-field signals, they report the values 33.49 and 18.22 ppm for the 1,4-trans polymer and 33.64 and 18.62 ppm for the 1,4-cis polymer (measured in $CDCl_3$ at room temperature and referred to $(CH_3)_4Si$). Our spectrum, obtained from that of a soluble copolymer with a high content of dimethylbutadiene and recorded under comparable conditions, is in good agreement with that of the 1,4-trans polymer and confirms the earlier structural attribution (Table V).

It is worth noticing that the chemical shift of atoms C1 and C2 in poly-D is very close to that of the same atoms in poly-B: this fact is due to a compensation between parameters of opposite sign. As regards the low-field region the shielding effect of the α' methyl on the unsaturated carbon (and not deshielding as is generally the case with α effects) is clearly shown by the shift of C2 from 134.80 to 128.81 ppm in passing from poly-I to poly-D (Figure 3).

In the saturated region the C1 signal of poly-D is centered precisely with respect to signals C1 and C4 of poly-I. If the chemical shift could be expressed in rigorously additive terms, this would necessarily lead to the coincidence of the C1 signals in poly-D and in poly-B. The difference between the two signals (0.62 ppm) must be considered to be a direct measure of the interaction between the methyl groups situated on the adjacent carbons C2 and C3.

A further measure of this interaction, this time with reference to the unsaturated carbons, can be obtained if we compare the C2 shift in passing from poly-I to poly-D (6.59 ppm) with that of C3 from poly-B to poly-I (5.68 ppm). The difference between the two values (0.91 ppm) is attributed in our scheme to the α'_T parameter, whose value differs from α' by 0.90 ppm.

These considerations, though of limited value in the interpretation of homopolymer spectra, have been found to be of great importance for a correct study of the spectra of diene copolymers, characterized by a high number of signals in very restricted areas of the spectrum.[35]

Experimental Section

Inclusion polymerization in PHTP was achieved as described in ref 3, 9, and 10 by direct polymerization or by using preirradiated PHTP. Inclusion copolymerization was carried out by direct polymerization in the presence of (3–10)-fold excess monomers. Polymers were separated from the PHTP matrix by extraction with boiling methanol.

The ^{13}C NMR spectra were obtained with a Varian XL 100 spectrometer operating in the FT mode under the following conditions: room temperature, solvent $CDCl_3$, concentration 5–10% (w/v), internal standard $(CH_3)_4Si$, spectral width 5000 Hz, pulse width 10 μs, data length 8192, sensitivity enhancement 0.4 s, transients 10000–50000; for quantitative measurements the pulse width was 30 μs and the delay time was 10 s.

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

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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

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