^{13}C nuclear magnetic resonance study of olefinic resonances in polymers containing regularly spaced double bonds. An incremental approach concerning neighbouring effects: application to polynorbornene

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Polymers with double bonds spaced regularly along the backbone (for example, 1,4-polybutadiene, polyalkenamers, polynorbornenes, etc.) show olefinic ^{13}C nuclear magnetic resonances, depending both on the carbon atom that is considered and on the configuration—*cis* or *trans*—of the neighbouring double bonds. Very different spectral features are observed. A general and simple formalism is proposed with a view to describing and measuring these neighbouring effects; it uses two additive incremental parameters of chemical shift variation. The relative values of these two parameters determine the spectral features of the olefinic resonances for a given polymer of that type. The different cases are discussed and polynorbornene is used here to illustrate the usefulness of this formalism.

(Keywords: double-bond configurational distribution; ^{13}C nuclear magnetic resonance; structure assignment; polynorbornene)

INTRODUCTION

In n.m.r. spectroscopy of organic compounds, differences in chemical shifts ($\Delta\delta$) between homologous products of a series have been used, via incremental methods, for structure prediction. In polymer analysis, this has been recognized as a valuable tool, mainly for polyolefins[1,2], to obtain detailed information about the structure of the chain, i.e. short- and long-chain branching in homo- and copolymers.

In a recent paper[3], we have used a similar incremental approach to describe and compare configurational and compositional effects on chemical shifts in homo- and copolymers. Here, we will briefly present the basis of the method concerning such effects and then extend the approach to neighbouring effects of double-bond configuration on olefinic chemical shift in polymers with regular unsaturation distributed all along the chain. This is illustrated by the discussion of the olefinic pattern in polynorbornenes observed at 50.3 MHz. Two random polynorbornenes, with respectively 20 and 50% *cis* content, are presented.

Extensive work has been done on this family of polymers for many years by Ivin *et al.*, including ^{13}C n.m.r. analysis[4–8]. The most recent paper[9] was published when the present work was under way. Olefinic assignments given here are in perfect agreement with Ivin's. It is satisfying that two quite different approaches lead to the same assignments.

METHOD

In ^{13}C n.m.r., a vinyl polymer is said to be sensitive to the tacticity at the triad level when the methinic CH exhibits three peaks related to the mm, mr + rm and rr triads. Generally, it was observed that:

$$\delta_{mr} - \delta_{mm} \sim \delta_{rr} - \delta_{rm}$$

This unique value for the differences in chemical shift may be written $\Delta\delta_{CF}$ and used as an incremental value. Depending on the nature of the polymer, the mm peak is either at higher (e.g. poly(vinyl chloride), PVC) or lower field (e.g. poly(vinyl alcohol), PVA). This configurational incremental value also depends, to a small extent, on the nature of the polymer. The meaning of $\Delta\delta_{CF}$ is the change in chemical shift of the central $C_\alpha H$ of a configurational triad when one of the constituent diads is changed from m to r:

$$\Delta\delta_{CF}(m \rightarrow r) = \Delta\delta_{CF} = -\Delta\delta_{CF}(r \rightarrow m)$$

$$\begin{tikzcd}
& \delta_0 = \delta_{mm} \arrow[dl, "+\Delta\delta_{CF}"'] \arrow[dr, "+\Delta\delta_{CF}"] & \\
\delta_{mr} \arrow[dr, "+\Delta\delta_{CF}"'] & & \delta_{rm} \arrow[dl, "+\Delta\delta_{CF}"] \\
& \delta_{rr} = \delta_0 + 2\Delta\delta_{CF} &
\end{tikzcd}$$

This approach is also of interest in a copolymer of A and B, to describe compositional effects at the triad level, in the absence of a configurational effect. In this case, three peaks are observed (AAA, AAB and BAB) in such

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an arrangement that:

$$\delta_{AAB}-\delta_{AAA}\sim\delta_{BAB}-\delta_{BAA}$$

so that a similar increment $\Delta\delta_{CP}$ is defined. It corresponds to the change in chemical shift of the central CH(A) when one of the neighbouring units is changed from A to B:

$$\begin{tikzcd}
& \delta_0=\delta_{AAA} \arrow[dl, "+\Delta\delta_{CP}"'] \arrow[dr, "+\Delta\delta_{CP}"] & \\
\delta_{AAB} \arrow[dr, "+\Delta\delta_{CP}"'] & & \delta_{BAA} \arrow[dl, "+\Delta\delta_{CP}"] \\
& \delta_{BAB}=\delta_0+2\Delta\delta_{CP} &
\end{tikzcd}$$

More generally in copolymers, both configurational and compositional effects on chemical shifts may be present. We have shown that spectral features can be described by a simultaneous combined use of $\Delta\delta_{CF}$ and $\Delta\delta_{CP}$ for styrene–butyl acrylate copolymers[3]. It should be noted that modified polymers may be considered as copolymers and be treated in the same way[10].

A new aspect of the possibilities of this method is applied here to the triad assignments—*cis* and *trans* double bonds—of norbornene polymers.

EXPERIMENTAL

Preparation of polymers

Two samples were examined, PN1 and PN2. PN1 is an industrial high molecular weight polynorbornene from CdF Chimie (Norsorex) obtained through ring-opening polymerization by a metathesis reaction in the presence of $RuCl_3$ as catalyst. Its limiting viscosity index in CCl_4 is $10\,\mathrm{dl\,g^{-1}}$ and the *cis/trans* ratio is 20/80.

PN2 is a laboratory-made polynorbornene[11] prepared by cross-metathesis with 1-pentene in the presence of a $W(NO)_2Cl_2$–$(P(Ph)_3)_2$ catalyst. Its limiting viscosity index in CCl_4 is $0.84\,\mathrm{dl\,g^{-1}}$ corresponding to $M=20\,000$. Infra-red analysis indicates a *cis/trans* ratio of 50/50. In PN1 and PN2, the total olefinic double-bond unsaturation is 90% of the theoretical amount.

^{13}C n.m.r. spectroscopy

Fourier Transform ^{13}C n.m.r. spectra were recorded at room temperature with a Bruker AM 200 operating at 50.3 MHz.

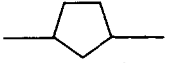
Polymer samples were examined at 15–20 wt% in $CDCl_3$ solvent. The flip angle was 30° and the repetition time was 0.9 s. A satisfactory signal-to-noise ratio was obtained, using from 10 000 to 20 000 pulses. Tetramethylsilane (TMS) was used as the internal reference.

RESULTS AND DISCUSSION

A polymer chain having the following general formula is considered:

$$\underset{\textit{cis or trans}}{-\mathrm{CH}=\mathrm{CH}-}[\;\mid\;]\underset{\textit{cis or trans}}{-\mathrm{CH}=\mathrm{CH}-}[\;\mid\;]\underset{\textit{cis or trans}}{-\mathrm{CH}=\mathrm{CH}-}$$

where [¦] represents a symmetric fragment, which means $-CH_2-CH_2-$ for 1,4-polybutadiene, $-CH_2-CH_2-CH_2-$ for polypentenamer and



for polynorbornene.

To distinguish successive double bonds, the Ivin terminology[8] will be used. Depending on the *cis* or *trans* neighbouring double bonds of a *trans* configuration, carbon atoms will be denoted as:

$$-\mathrm{CH}\overset{t}{=}\mathrm{CH}-[\;\mid\;]-\underset{ttt}{\mathrm{CH}}\overset{t}{=}\underset{ttt}{\mathrm{CH}}-[\;\mid\;]-\mathrm{CH}\overset{t}{=}\mathrm{CH}-$$

$$-\mathrm{CH}\overset{t}{=}\mathrm{CH}-[\;\mid\;]-\underset{ttc}{\mathrm{CH}}\overset{t}{=}\underset{ctt}{\mathrm{CH}}-[\;\mid\;]-\mathrm{CH}\overset{c}{=}\mathrm{CH}-$$

$$-\mathrm{CH}\overset{c}{=}\mathrm{CH}-[\;\mid\;]-\underset{ctc}{\mathrm{CH}}\overset{t}{=}\underset{ctc}{\mathrm{CH}}-[\;\mid\;]-\mathrm{CH}\overset{c}{=}\mathrm{CH}-$$

The carbons in *cis* centred triads may be similarly defined. It may be seen that the central letter refers to the central double bond, the first one to the nearest double bond and the third to the structure of the remote double bond. There is an equal number of carbon atoms denoted by *ttc* and *ctt* respectively. These atoms are not magnetically equivalent.

Let δ_0 be the chemical shift of vinyl carbon *ttt*. Then $\Delta\delta_n$ is the change in chemical shift due to the change from configuration *t* to *c* of the nearest (n) double bond. Similarly, $\Delta\delta_r$ corresponds to the remote (r) double bond. $\Delta\delta$ is an algebraic value. The different chemical shifts are related as follows:

$$\begin{tikzcd}
& \delta_{ttt}=\delta_0 \arrow[dl, "+\Delta\delta_r"'] \arrow[dr, "+\Delta\delta_n"] & \\
\delta_{ttc}=\delta_0+\Delta\delta_r \arrow[dr, "+\Delta\delta_n"'] & & \delta_{ctt}=\delta_0+\Delta\delta_n \arrow[dl, "+\Delta\delta_r"] \\
& \delta_{ctc}=\delta_0+\Delta\delta_n+\Delta\delta_r &
\end{tikzcd}$$

This means that, to get *ctt* from *ttc*, the nearest double bond must be changed from *trans* to *cis* (*t*→*c*) and the reverse for the other double bond (*c*→*t*), so:

$$\delta_{ctt}=\delta_{ttc}+\Delta\delta_n-\Delta\delta_r$$

In a similar way, *ctc* is obtained from *ttt* by changing the two neighbouring double bonds from *trans* to *cis* (*t*→*c*)

$$\delta_{ctc}=\delta_{ttt}+\Delta\delta_n-\Delta\delta_r$$

It can be seen that several cases are possible, according to the respective $\Delta\delta_r$ and $\Delta\delta_n$ values. We will now examine these different cases.

Case 1: $\Delta\delta_r=\Delta\delta_n=0$. In this case, the nature of the neighbouring double bonds has no effect on the chemical shift of the olefinic carbons of a *trans* unit. The same will hold for *cis* double bonds. The consequence is a unique peak for *trans* structure with a chemical shift:

$$\delta_0=\delta_{ttt}=\delta_{ttc}=\delta_{ctt}=\delta_{ctc}=\delta_t$$

The unique peak corresponding to *cis* structure has a chemical shift δ_c. Consequently, no information can be obtained on the distribution of double-bond configuration.

Table 1 Relative peak intensities of a triad when $\Delta\delta_r \sim \Delta\delta_n$

	P_t	P_{ttt} $=P_t^2$	$P_{ttc+ctt}$ $=2P_t(1-P_t)$	P_{ctc} $=(1-P_t)^2$
PN1	0.80	0.64	0.32	0.04
PN2	0.50	0.25	0.50	0.25

Table 2 Relative peak intensities of a configurational triad when $\Delta\delta_r = -\Delta\delta_n$

	P_t	P_{ttc} $=P_t(1-P_t)$	$P_{ttt+ctc}$ $=P_t^2+(1-P_t)^2$	P_{ctt} $=P_t(1-P_t)$
PN1	0.80	0.16	0.68	0.16
PN2	0.50	0.25	0.50	0.25

Case 2: $\Delta\delta_r \sim \Delta\delta_n \neq 0$. The spectrum is composed of three peaks corresponding to *ttt*, *ttc*+*cct* and *ctc*:

$$\delta_{ttt} = \delta_0$$
$$\delta_{ttc} = \delta_{ctt} = \delta_0 + \Delta\delta_r = \delta_0 + \Delta\delta_n$$
$$\delta_{ctc} = \delta_0 + 2\Delta\delta_r = \delta_0 + 2\Delta\delta_n$$

Knowing the total amount of *trans* double bonds, and applying classical probability rules for Bernoullian statistics, the relative intensities of peaks of a *trans* centred triad may be calculated as in *Table 1*. For a polymer having a *cis*/*trans* ratio close to 1, the intensities are 1:2:1 so that the three peaks appear as a triplet. For higher *trans* content $I_{ttt} > I_{ttc+ctt} > I_{ctc}$, and the reverse holds at a lower content. It can be seen here that information can be obtained.

Case 3: $\Delta\delta_r \sim -\Delta\delta_n \neq 0$. The spectrum of *trans* vinyl carbon (also *cis*) is once more composed of three peaks: *ttt*+*ctc* (central peak), *ttc* and *ctt*:

$$\delta_{ttt} = \delta_0 = \delta_{ctc}$$
$$\delta_{ttc} = \delta_0 + \Delta\delta_r = \delta_0 - \Delta\delta_n$$
$$\delta_{ctt} = \delta_0 + \Delta\delta_n = \delta_0 - \Delta\delta_r$$

While *ttt* and *ctc* carbon atoms are not magnetically equivalent, they have the same chemical shift since configuration changes of neighbouring double bonds have equal but opposite values. The same probability calculation as in case 2 gives the relative peak intensities in *Table 2*. It appears that the spectrum is quite different from that in case 2, except for 1/1 *cis*/*trans*, where both hypotheses, with quite different assignments, lead to the same spectrum. In this case 3, when the *trans* content is varied, the general aspect of the spectrum is unchanged: symmetrical, with a main central peak and two wings.

Case 4: $|\Delta\delta_r| \neq |\Delta\delta_n|$. In this case $\delta_{ttt} \neq \delta_{ctc}$ so that the spectrum is composed of four peaks for *cis* and *trans* centred triads. Depending on the relative values of $\Delta\delta_r$ and $\Delta\delta_n$, four cases may be encountered.

(a) $|\Delta\delta_n| < |\Delta\delta_r|$, both positive or negative. According to definitions in case 2, the order of peaks is *ttt*, *ttc*, *ctt*, *ctc*, with δ_0 either at higher or lower field.

(b) $|\Delta\delta_n| > |\Delta\delta_r|$, both positive or negative. The order is changed for the two central peaks: *ttt*, *ctt*, *ttc*, *ctc*.

(c) $|\Delta\delta_n| < |\Delta\delta_r|$, with opposite signs. The order is now *ctt*, *ttt*, *ctc*, *ttc*.

(d) $|\Delta\delta_n| > |\Delta\delta_r|$, with opposite signs. The four peaks are in the following order: *ctt*, *ctc*, *ttt*, *ttc*.

In the first two cases, the two central peaks have equal intensities, whereas in the last two cases, equal intensities are observed for lateral peaks.

Case 5: $\Delta\delta_r = 0$ *and* $\Delta\delta_n \neq 0$. Only the nearest double-bond configuration has any effect, so that two peaks are obtained in the *trans* olefinic carbon spectrum:

$$\delta_{ttt} = \delta_{ttc} = \delta_0$$
$$\delta_{ctt} = \delta_{ctc} = \delta_0 + \Delta\delta_n$$

respectively denoted $\delta_{\underline{t}t}$ and $\delta_{c\underline{t}}$. The same holds for the two *cis* peaks, $\delta_{\underline{c}c}$ and $\delta_{t\underline{c}}$.

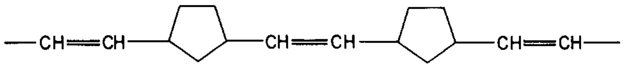
Case 6: $\Delta\delta_n = 0$ *and* $\Delta\delta_r \neq 0$. The nearest double-bond configuration has no effect, so that the *trans* triad spectrum has two peaks:

$$\delta_{ttt} = \delta_{ctt} = \delta_0 = \delta_{\underline{t}t}$$
$$\delta_{ttc} = \delta_{ctc} = \delta_0 + \Delta\delta_r = \delta_{\underline{t}c}$$

Underlined $\underline{t}$ indicates the *trans* configuration of the considered double bond. The neighbouring double-bond configuration is indicated before or after, respectively for the nearest and remote double bond, so that analogy with Ivin's notation is maintained[8].

Let us examine now 1,4-polybutadiene which was studied by ^{13}C n.m.r. at 25.10 MHz some years ago[12]. Vinyl carbon atoms give a spectrum with two *cis* peaks and two *trans* peaks (*Table 3*). Analysis of polymers with different *trans* contents indicates that they obey case 6. This means that $\Delta\delta_n = 0$ and $\Delta\delta_r = 0.08$ and 0.17 ppm respectively for effect on a *trans* or *cis* carbon.

Let us consider now the spectrum of another polymer, polynorbornene:



at 50.3 MHz (*Figure 1*). The *trans* vinyl carbon atoms appear as three peaks, which refer to cases 2 or 3, where both neighbouring double bonds equally affect the chemical shift of the central unit $|\Delta\delta_r| = |\Delta\delta_n|$. From *Tables 1* and *2*, it can be seen that the *cis*/*trans* ratio must be different from 1 to distinguish cases 2 and 3, so that we

Table 3 Chemical shifts and assignments of vinyl carbon atoms in 1,4-polybutadiene[12]

Central double bond	Peak number	δ (ppm)	Assignment[12]	Increment values (ppm)
Trans	4	130.37	$t\underline{t}c$ and $c\underline{t}c$, i.e. tc	$\Delta\delta_n = 0$
	3	130.29	$c\underline{t}t$ and $t\underline{t}c$, i.e. $\underline{t}t$	$\Delta\delta_r = 0.08$
Cis	2	129.87	$t\underline{c}c$ and $c\underline{c}c$, i.e. $\underline{c}c$	$\Delta\delta_n = 0$
	1	129.70	$c\underline{c}t$ and $t\underline{c}t$, i.e. $\underline{c}t$	$\Delta\delta_r = 0.17$

Table 4 Chemical shifts[a], assignments[a] and increment values[b] in polynorbornene (observed at 50.3 MHz)

Central double bond	Peak number	δ (ppm) trans/cis ratio 80/20	δ (ppm) trans/cis ratio 50/50	Assignment[a]	Increment values[b] (ppm)
Cis	7	134.18	134.15	*tcc*	$\Delta\delta_n = -0.15$ [−0.16]
	6	134.10	134.06	*tct*	$\Delta\delta_n + \Delta\delta_r = -0.06$
	5	–	134.00	*ccc*	
	4	133.93	133.90	*cct*	$\Delta\delta_r = 0.10$ [0.09]
Trans	3	133.29	133.25	*ttc*	$\Delta\delta_r = 0.12$ [0.12]
	2	133.17	133.13	*ttt + ctc*	$\Delta\delta_n + \Delta\delta_r = -0.04 \simeq 0$
	1	133.00	132.97	*ctt*	$\Delta\delta_n = -0.16$ [−0.17]

[a] These assignments are identical to those published by Greene[9]; chemical shifts are about 0.25 ppm lower
[b] In square brackets, increment values are calculated from Greene's results[9]

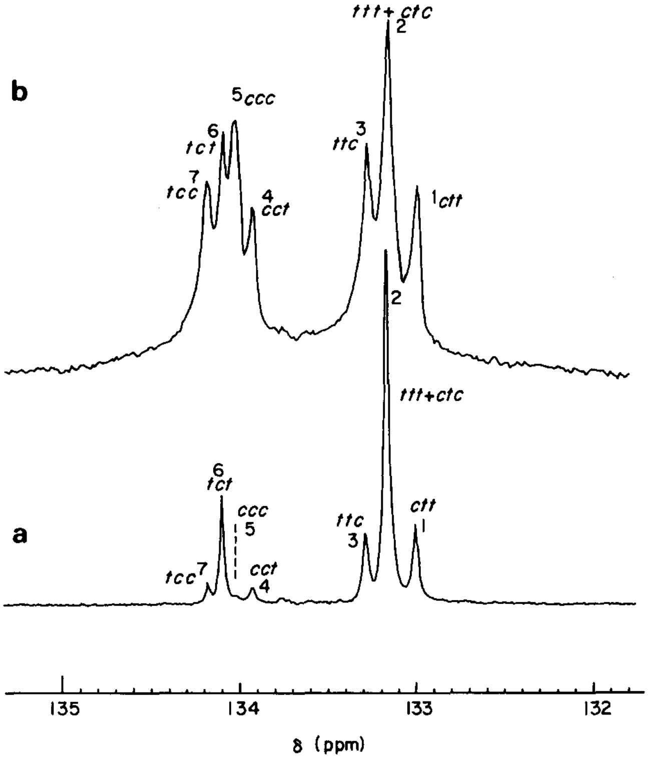


Figure 1 ^{13}C n.m.r. spectrum (50.3 MHz); enlargement of olefinic resonances in polynorbornenes: *trans/cis* ratio is (a) 80/20 and (b) 50/50

turn to PN1. We see that the symmetry and the relative peak intensities are in agreement with case 3, where $\Delta\delta_r$ is almost equal to $-\Delta\delta_n$. The central peak is due to *ttt* + *ctc* triads (*Table 4*). The *cis* vinyl carbons have four resonance peaks at 50.3 MHz. The lateral peaks have nearly equal intensities and may be attributed to triads *tcc* and *cct*. As for the two central peaks, the one at higher field may be attributed to triad *ccc*, since its intensity is very low for a 20% *cis* polymer. In *Table 4* values of $\Delta\delta_r$ and $\Delta\delta_n$ are given for *cis* and *trans* double bonds.

As pointed out by Greene[9], assignment of peaks 1 and 3 or 4 and 7 is not easy, since—in a symmetrical polynorbornene—intensities are the same, whatever the *cis/trans* ratio. In the case of an asymmetric polymer of the same family (2-methylnorbornene), it was proved[8] that *tcc* and *ttc* were more deshielded than *cct* and *ctt* respectively. Greene assumes the same line order in polynorbornene[9]. Using the incremental approach, we come to the same assignment, assuming that $\Delta\delta_r$ has the same sign as in 1,4-polybutadiene. In this polymer, it is observed that the change from *trans* to *cis* of the remote double bond (through four C atoms with a double bond) leads to an increase in chemical shift. Applying this to polynorbornene (through five C atoms with a double bond), peaks 1 and 3 may be assigned to *ctt* and *ttc* respectively, so that 4 and 7 represent *cct* and *tcc* triads. Calculated incremental values from Greene's results[9] are in excellent agreement with our results. Ivin's results[8] on 2-methylnorbornene give $\Delta\delta_r = -\Delta\delta_n = 0.20$ ppm for both *cis* and *trans* double bonds. It can be seen that substitution in position 2 has little effect on $\Delta\delta$ values. The incremental approach presented here clearly shows that a *cis* content different from 50% is necessary to distinguish between the different possibilities, leading to apparent triplet spectra. Among the two possibilities, only lower *cis* contents—i.e. random polymers—can discriminate, so we chose 20%. Higher *cis* contents result in a stereoselective mechanism.

CONCLUSION

We have correlated the olefinic *trans* (and *cis*) ^{13}C chemical shifts in polynorbornene with respect to the configuration (*cis* or *trans*) of their two neighbouring double bonds, using a general formalism that is presented. This formalism introduces two additive parameters of chemical shift variation and can also be used for all polymers presenting regularly spaced double bonds along the chain, particularly for polyalkenamers. Concerning this class of polymers, a ^{13}C n.m.r. study of methylene carbon resonances was done by H. Y. Chen[13], and results were published by Ivin[6] on copolymers of cyclopentene and norbornene, including olefinic resonance patterns.

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