

^{13}C n.m.r. spectra of polymers made by ring-opening polymerization of (\pm)- and (+)-exo-5-methylbicyclo[2.2.1]hept-2-ene using metathesis catalysts

Kenneth J. Ivin, Grzegorz Łapienis* and John J. Rooney

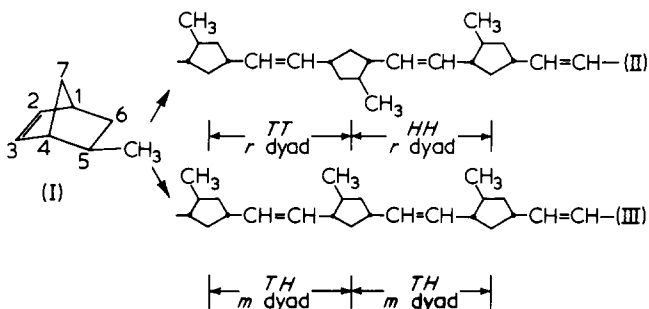
Department of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, UK

(Received 10 September 1979; revised 25 October)

A range of olefin metathesis catalysts has been used to prepare ring-opened polymers of (\pm)- and (+)-exo-5-methylbicyclo[2.2.1]hept-2-ene, (I), having *cis* double bond contents of 11–100%. The ^{13}C n.m.r. spectra of these polymers are interpreted in terms of *TH*, *TT*, *HH*, *HT* and *tt*, *tc*, *ct*, *cc* structures (*T* = tail, *H* = head, referring to methyl groups; *t* = *trans*, *c* = *cis*, referring to double bonds). The all-*cis* polymer has a fully-syndiotactic ring sequence, but polymers with less than 55% *cis* double bonds have an atactic ring sequence. The substitution shift parameters indicate that the cyclopentane rings in the polymer chain adopt the puckered conformation which minimizes non-bonded repulsion between the *cis*-1,3-olefinic substituents.

INTRODUCTION

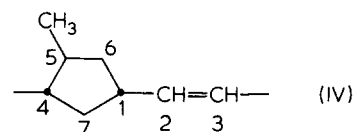
As we have reported briefly¹ the all-*cis* polymer made by ring-opening polymerization of (+)-(I) initiated by ReCl_5 , has a fully syndiotactic ring sequence II in which the methyl groups are disposed alternately tail–tail (*TT*) and head–head (*HH*). The presence of (–)-enantiomer in the monomer results in the formation of *HT* and *TH* structures, in addition to *HH* and *TT*. No conditions have been found for the production of fully isotactic polymers III but in high-*cis* polymers the *trans* double bonds tend to be associated with isotactic dyads. Polymers having less than 55% *cis* double bond content have an atactic ring sequence, i.e. equal proportions of *m* and *r* dyads.



The mechanistic significance of these observations has been discussed elsewhere¹. Here we present a detailed analysis of the complete ^{13}C n.m.r. spectra in which fine structure derives not only from the *TH*, *TT*, *HH*, *HT* effect, but also from sensitivity to adjacent double bond structures.

In the present paper the carbon atoms in the polymer unit IV will be numbered as in the monomer, rather than according to their position in the ^{13}C n.m.r. spectrum.

* On leave from the Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Łódź, Poland



It should be noted that in the ^{13}C n.m.r. spectrum of polynorbornene² C^5 and C^6 were previously labelled C^1 , C^1 and C^4 were labelled C^2 ; C^7 was labelled C^3 ; and C^2 and C^3 were labelled C^4 . When the symbols *TH*, *TT*, *HH*, *HT* are used to designate carbon atoms, the first letter will denote the orientation of the methyl group on the nearer of the two rings in the dyad. It should be noted that C^1 , C^2 , C^6 are always part of a tail, and C^3 , C^4 always part of a head structure. Likewise, olefinic carbons and carbon atoms located between two double bonds will be designated *tt*, *tc*, *ct* or *cc*, the first letter indicating the *trans* or *cis* structure of the nearer double bond. σ_c will denote the fraction of double bonds having *cis* structure.

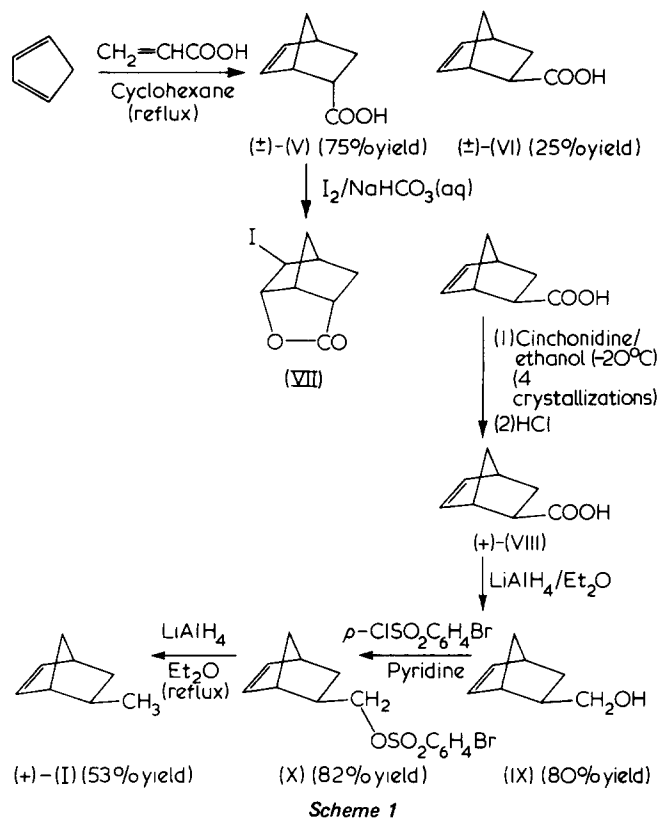
EXPERIMENTAL

Preparation of monomer

The six-stage procedure for the preparation of (+)-(I) is shown in Scheme 1. The first stage was conducted in refluxing cyclohexane in order to enhance the yield of exo acid. The product acids were separated from cyclohexane (and the slight excess of cyclopentadiene) by extraction with aqueous NaOH, followed by acidification and extraction with chloroform. Yields were close to 100% and the product contained 25–30% exo acid as determined by ^{13}C n.m.r.

The endo acid V was removed from the endo/exo mixture by conversion to its iodolactone³ and the exo acid VI then resolved by triangular fractional crystallization of its cin-

chonidine salts in ethanol⁴. Four stages of crystallization and combination of two head fractions gave, on acidification, an impure sample of exo acid with an apparent optical purity of 58%. Subsequent results on the all-cis syndiotactic polymer showed that this acid must have had an optical purity of at least 73%. The conversion of VIII to I



followed standard procedures, the intermediate alcohol IX having b.p. 86°/8.5 mmHg. The final product, I, was distilled over sodium through a short column, b.p. 114°–116°C, $[\alpha]_D^{25} = 17.8^\circ$ (ethanol, $c = 6.15 \text{ g dl}^{-1}$), estimated optical purity 73% (see above), estimated chemical purity 88% (¹³C n.m.r.); 3.5 kg of V/VI mixture gave 19 g (+)-(I). Further purification of I was not attempted because of the small amount of material and because tests showed that it would readily undergo ring-opening polymerization. ¹³C chemical shifts of various compounds in Scheme 1 are recorded in Table 1.

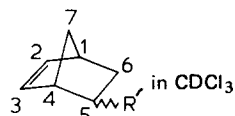
Polymerization of monomer

Table 2 gives a summary of the catalyst systems used to prepare a range of polymers having different values of σ_c . Polymerizations were normally carried out under dry nitrogen in flasks closed with serum caps. Reaction mixtures generally became quite viscous and reaction was terminated by addition of ethanol. Sometimes the recovered material would not dissolve in CDCl₃ but would swell sufficiently to give a well-resolved ¹³C n.m.r. spectrum.

¹³C n.m.r. spectra

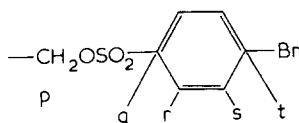
These were mostly obtained at 22.63 MHz using a PFT Bruker WH90 instrument, with complete decoupling of protons. Typical operating conditions were: spectral window 4000 Hz, 2000–60 000 pulses of length 10 μ s, acquisition time 1.02 s, 8K data points (FID) transforming to 4K points in the plotted spectrum (1 channel = 0.043 ppm). A few spectra were also obtained at 75 MHz by courtesy of Dr F. Heatley (University of Manchester, UK). The positions of all peaks are reported downfield from TMS.

Table 1 ¹³C chemical shifts^a of some norbornene derivatives



R:	exo-CH ₃	exo-CH ₂ OH	exo-CH ₂ OR	exo-COOH	endo-COOH
C ¹	42.29 (42.7)	41.56 ^b [41.0]	41.60	41.72 [42.0]	43.48 [43.1]
C ²	137.06 ^b (137.2)	136.80 ^b [137.7]	137.14 ^b	138.10 ^b [135.2]	137.78 ^b [134.9]
C ³	135.98 ^b (136.2)	136.54 ^b [137.0]	135.89 ^b	135.76 ^b [134.5]	132.58 ^b [130.7]
C ⁴	48.29 (48.7)	43.37 [42.8]	43.37	46.73 [46.8]	45.75 [46.4]
C ⁵	32.54 (33.0)	41.82 ^b [41.5]	38.28	43.28 [42.2]	42.63 [41.7]
C ⁶	34.57 (35.0)	29.65 [29.5]	29.39	30.35 [29.9]	29.18 [27.3]
C ⁷	44.79 (45.0)	44.97 [45.2]	44.84	46.40 [47.0]	49.78 [50.7]
R'	21.58 (21.7)	67.23	74.87 (p) 135.46 ^c (q) 129.33 ^b (r) 132.61 ^b (s) 128.86 ^c (t)	183.01	181.52

^a Values in round brackets are from the literature⁵. Those in square brackets are predicted by the use of substitution parameters
^b Assignment is uncertain because of the proximity of another line
^c Weak intensity: assignments by comparison with bromobenzene and acetophenone;



^d The iodolactone VII had the following ¹³C chemical shifts (numbering corresponds to the formula at head of Table with I atom attached at C² and O at C³): 179.11 (C=O), 88.91 (C³), 46.79, 46.53 (C¹ and C⁴), 37.30 (C⁵ and C⁷), 34.51 (C⁶), 29.90 (C²). The following values were observed in C₆D₆: 88.45 (C³), 46.79, 46.27 (C¹ and C⁴), 37.17 (C⁵), 37.04 (C⁷), 33.99 (C⁶), 30.55 (C²); (C=O not detected)

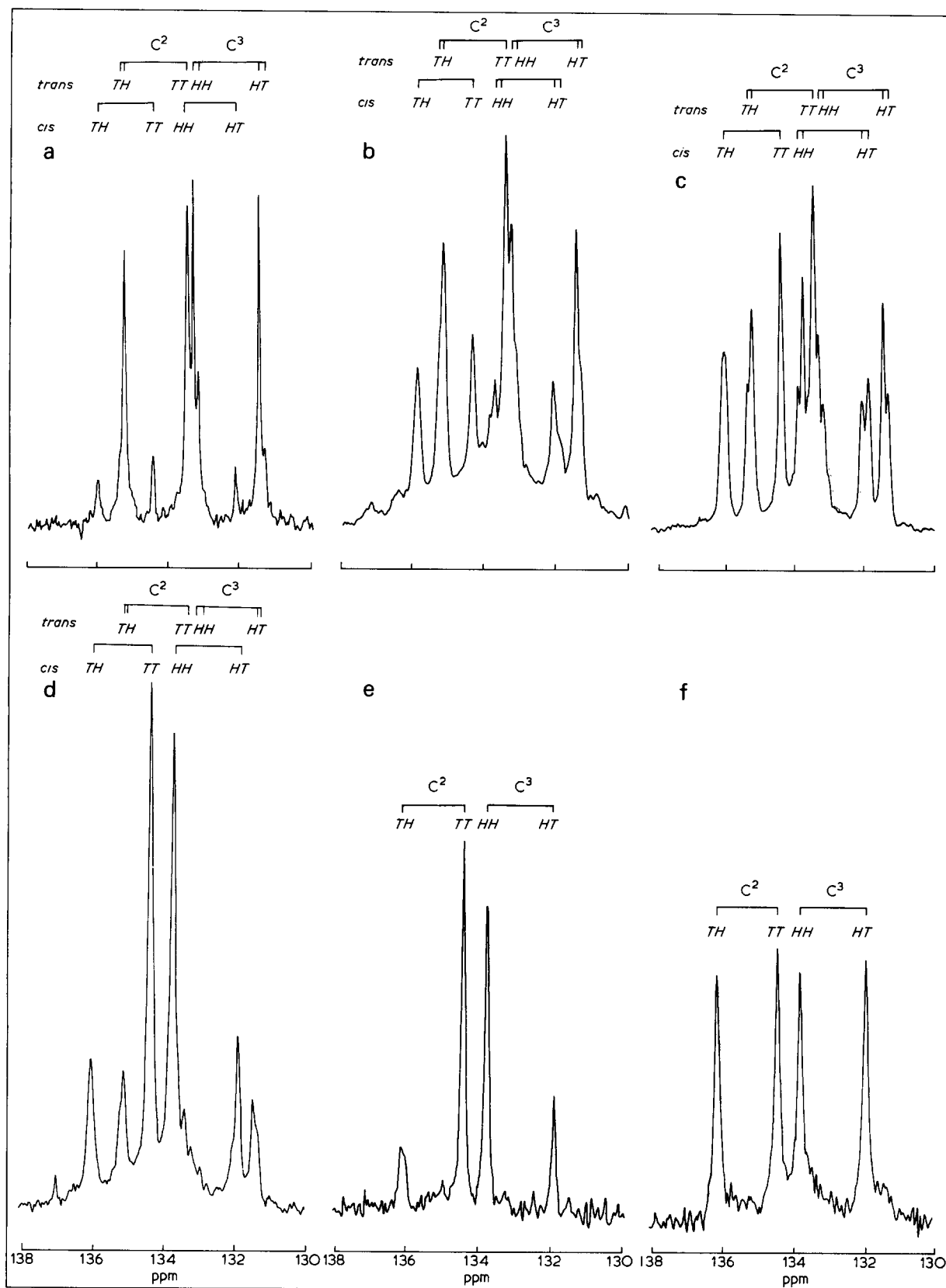


Figure 1 ¹³C n.m.r. spectra (olefinic region) of polymers made from (a) (+)*- or (±)-monomer, $\sigma_C = 0.11$; (b) (+)*- or (±)-monomer, $\sigma_C = 0.25$; (c) (+)*- or (±)-monomer, $\sigma_C = 0.52$; (d) (+)-monomer, $\sigma_C = 0.74$; (e) (+)-monomer, $\sigma_C = 1.0$; (f) (±)-monomer, $\sigma_C = 1.0$. See Table 2. Asterisk denotes the spectrum actually displayed. (a) was obtained at 75 MHz; the others at 22.63 MHz

RESULTS AND DISCUSSION

Each spectrum of the polymer has a group of olefinic carbon peaks (131–137 ppm), a group of ring-carbon peaks (35–53 ppm) and a methyl carbon resonance (19 ppm). We

consider first the assignment of the olefinic carbons, leading on to the determination of tacticity. After discussing the fine structure of the olefinic region we come first to the basic assignment of the ring-carbon resonances and then to their fine structure.

Olefinic carbons

Figures 1a–e show the olefinic region for five polymers prepared as indicated in Table 2. For (a), (b) and (c) ($\sigma_c = 0.11$ – 0.52) the spectra are essentially independent of whether (+)- or (±)-monomer is used to prepare the polymer. However, for the all-*cis* polymer made from (±)-monomer, the spectrum, shown in Figure 1f, is markedly different from that made from (+)-monomer, Figure 1e.

Figure 1f consists of four equally intense lines, corresponding to equal proportions of *TH*, *TT*, *HH* and *HT* olefinic carbons as expected for a polymer made from (±)-monomer. The assignment can be made on the basis of the expected shifts caused by methyl substitution in polynorbornene. Defining the substitution parameters as γ , δ_1 and δ_2 (see Table 3), the four lines are expected to be displaced from that for polynorbornene by $\delta_1 + \delta_2$ (*TH*), δ_1 (*TT*), $\delta_2 + \gamma$ (*HH*) and γ (*HT*). The four lines for *cis* double bonds should therefore show a symmetrical pattern with the separation between *TH* and *TT* the same as between *HH* and *HT*, as indeed is observed. With normal values of δ and γ the lines can be expected to be in the order *TH*, *TT*, *HH*, *HT* (downfield to upfield) but there is slight uncertainty about the relative order of *TT* and *HH* for the *trans* resonances, see Figure 1a, where the separation of the *TT*

and *HH* lines is only 0.17 ppm. However, the δ_1 values (Table 3) show best consistency if the line order is always the same: *TH*, *TT*, *HH*, *HT*. The larger negative values of γ for polymer made from endo-monomer (Table 3) is clearly a consequence of the *cis* relationship of the Me– and –CH=CH– groups attached to the cyclopentane ring. In the polymer of the exo-monomer these have a *trans* relationship which will reduce the interaction between them.

The above assignments allow us to proceed to the determination of tacticity. In Figure 1e the *TT*, *HH* structures are clearly much preferred (*HH/HT* = *TT/TH* = 3.29) and the relative intensities are consistent with an all-*cis* polymer having a fully syndiotactic ring sequence incorporating 13.5% units derived from (–)-enantiomer. It is most unlikely that the optical purity was higher than 73% [(+)/(–) = 86.5/13.5] since the loss of syndiotacticity that would then have been required to explain the observed spectrum would almost certainly have been accompanied by the formation of a proportion of *trans* double bonds. This argument is supported by the fact that the spectrum of the polymer having $\sigma_c = 0.74$, Figure 1d, does show some loss of syndiotacticity about the *cis* double bonds. In this case *HH/HT* = *TT/TH* = 2.6. The corresponding ratio for the *trans* double bonds is not easy to determine precisely because of overlap and fine structure of the central peaks, but qualitatively it seems clear that in this case *HT/HH* = *TH/TT* > 1, the value being comparable with *HH/HT* for *cis* double bonds. In other words in high-*cis* polymers, *cis* double bonds are associated mainly with *r* dyads and *trans* double bonds mainly with *m* dyads. Here we use this information to make detailed assignments. The mechanistic significance is discussed elsewhere¹.

For the polymers with $\sigma_c < 0.55$ the four *cis* resonances are all equal as also are the four *trans* resonances, regardless of whether the polymer is made from (+)- or (±)-monomer; see Figures 1a, 1b and 1c. This shows that in these polymers the ring sequence is completely atactic. This knowledge is useful in distinguishing fine structure due to *TH*, *TT*, *HH*, *HT* from that due to *tt*, *tc*, *ct*, *cc* in the upfield region.

Finally in this section we consider the fine structure of the olefinic *TH*, *TT*, *HH*, *HT* lines arising from *cis/trans* effects. Table 4 shows the assignments based on an examination of the intensity relationships in all the spectra. This assignment is assisted by the knowledge that at low σ_c the

Table 2 Catalyst systems for ring-opening polymerization of (+)–(I)

Catalyst system ^a	Solvent	σ_c ^b	Notes
RuCl ₃ /COD complex ^c	PhCl	0.11	
IrCl ₃ /COD complex ^d	PhCl	0.25	
WCl ₆ /EtAlCl ₂ (1/4)	C ₆ H ₆	0.52	Add EtAlCl ₂ last
WCl ₆ /n-Bu ₄ Sn (1/2)	C ₆ H ₆	0.74	Premix catalyst components
ReCl ₅	C ₆ H ₆	1.0	Use high monomer concn. (5.9 mol litre ⁻¹)

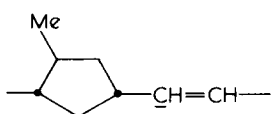
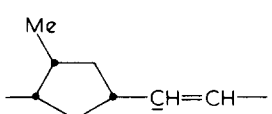
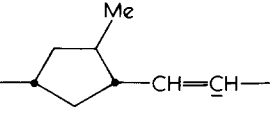
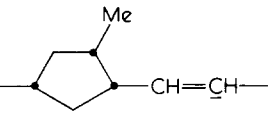
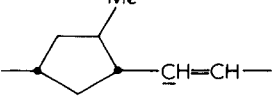
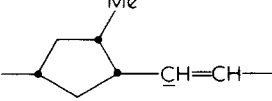
^a Details of typical reaction conditions have been given in previous papers^{2,6,7}

^b Fraction of *cis* double bonds determined from C⁴ peak areas (see IV)

^c Prepared by heating 1 g RuCl₃·xH₂O, 12.5 cm³ H₂O, 7.5 cm³ EtOH, 2 cm³ *cis,cis*-cycloocta-1,5-diene (COD) for 8 days at 50°C, after which the volatiles were removed, the residue washed with ethanol and dried; yield 1.4 g

^d Prepared in a similar manner to RuCl₃/COD complex starting from IrCl₃·xH₂O

Table 3 ¹³C shift parameters^a in ppm for the effect of 5-methyl substitution on the olefin carbons in the polymer of norbornene^b

Polymer from exo-monomer		Polymer from endo-monomer ⁶	
	δ_1 (<i>cis</i>) = 0.54 δ_1 (<i>trans</i>) = 0.33		δ_1 (<i>cis</i>) = 0.55 δ_1 (<i>trans</i>) = 0.39
	δ_2 (<i>cis</i>) = 1.81 ^c δ_2 (<i>trans</i>) = 1.77 ^c		δ_2 (<i>cis</i>) = 0.75 ^c δ_2 (<i>trans</i>) = 1.42 ^c
	γ (<i>cis</i>) = -1.87 γ (<i>trans</i>) = -1.61		γ (<i>cis</i>) = -3.28 γ (<i>trans</i>) = -2.79

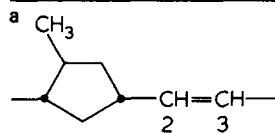
^a γ , δ_1 , δ_2 indicate the effect on the shift of the underlined atom

^b Based on an assumed line order *TH*, *TT*, *HH*, *HT*

^c Average spacing between *TH* and *TT* on the one hand, and *HH* and *HT* on the other

Table 4 Assignment of olefinic peaks in polymers^a of I

Position (ppm)	Assignment	Position (ppm)	Assignment		
136.15	cc } TH } C ²	135.29	tc } TH } C ²		
136.02		ct } TT }		135.16	tt }
134.42		cc/ct }		133.43	tt/tc }
133.95	ct } HH } C ³	133.26	tt } HH } C ³		
133.82		cc }		133.13	tc }
132.09		ct }		131.45	tt }
131.92		cc }		131.32	tc }



cis and *trans* double bonds are likely to be distributed at random as in polynorbornene⁷ so that the ratios *tt/tc* and *ct/cc* are both greater than unity, whereas at high σ_c , *tt/tc* remains greater than or equal to unity while *ct/cc* is less than unity.

C² (*TT, c*) gives a single peak for all polymers and provides a convenient reference. The four *cc* peaks are those in Figures 1e and 1f while the four *tt* peaks are the main peaks in Figure 1a. The *ct* peaks are the main *cis* peaks in polymers of low σ_c . A notable feature of Figure 1a is the rather sharp resolution of the *tt* and *tc* peaks for C³ (*HH*), with the *tt/tc* ratio appearing to be somewhat smaller for *HH* than for *TH* and *HT*. The fact that neither of the resonances at 134.42 and 133.43 ppm shows fine structure tends to confirm that the latter is correctly assigned to *TT* (*t*); see earlier discussion concerning the *TT, HH* line order. The splittings for the other three pairs of lines (Table 4) are comparable with those observed² for polynorbornene (0.13 ppm). The fine structure for *TH, HT* also forms a regular pattern: *cc, ct; ct, cc* for *cis*, and *tc, tt; tt, tc* for *trans*.

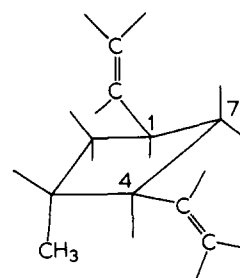
Ring carbons

Figures 2a–2f show the ring-carbon region for the spectra of the same polymers as those whose olefinic regions were shown in Figures 1a–1f, respectively. The line positions and assignments for the all-*cis* and the high-*trans* polymers are listed separately in Tables 5 and 6. We first consider the assignment of the groups of peaks to the five carbon atoms and then the fine structure within each group.

The lines between 40 and 43 ppm are too closely bunched to make off-resonance experiments very informative, but with full ¹H coupling it is possible to distinguish the CH and CH₂ resonances in the all-*cis* and high-*trans* polymers. The CH carbons C¹ C⁴, which are α to the double bond, can be assigned unambiguously for the all-*cis* polymer from their line positions in the spectrum; likewise for C⁴ in the high-*trans* polymer. The difference in the two C⁴ chemical shifts (*trans* minus *cis*) amounts to 52.2–47.5 = 4.7 ppm, characteristic of carbons α to the double bond. Assuming the same difference for C¹ leads us to expect C¹(*trans*) at 36.0 + 4.7 = 40.7 ppm; hence the assignment of the peaks at 40.69, 40.56 in the high-*trans* polymer to C¹ (*trans*). The third CH resonance can then be assigned to C⁵ in each case (*cis* 40.7; *trans* 39.8) giving α -substitution parameters of 7.5 and 7.4 ppm, respectively.

The assignment of the CH₂ resonances presents more of

a problem. However, one is assisted by the fact that another group of resonances appears at 42.1–42.6 ppm in the spectra of polymers of intermediate σ_c . This group lies between the 42.8–43.2 group in the all-*cis* polymer and the 41.7–41.9 group in the high-*trans* polymer, with an average splitting of 0.6 ppm between the groups. This behaviour is exactly the same as observed in the spectrum of polynorbornene² for the carbon corresponding to C⁷, the centre group (peak) being derived from *ct/tc* structures. By elimination the remaining resonances at 41.99 (*cis*) and 41.08, 40.95 (*trans*) are assigned to C⁶, giving β -substitution parameters of 8.8 and 8.7 ppm, respectively, in good agreement with those derived from the C⁴ resonances (8.9 and 9.1 ppm, respectively). The only surprising feature of this assignment is that the C⁷ line positions correspond to ($\gamma + \delta$)-substitution parameters which are positive (0.3 and 0.4 ppm, respectively) whereas the C¹ line positions give the expected negative values (–2.6 and –2.5 ppm, respectively). This suggests that in the case of C⁷ the *gauche* interaction with the methyl group is reduced by puckering of the ring so as to relieve the non-bonded repulsion between the *cis*-1,3-olefinic substituents (C¹ and C⁴ positions in XI and IV).



(XI)

The fine structure within each group of peaks may now be considered, proceeding from downfield to upfield. For the all-*cis* polymer this can only arise from head–tail effects. The assignment of the two C⁴ (*cc*) peaks in Figure 2f to *HH, HT* can readily be made from their relative intensities in Figure 2e, knowing from Figure 1e that *HH* > *HT*. In the high-*trans* polymer C⁴ (*trans*) shows two strong peaks (52.35, 52.09) assigned to *tt* (*HH, HT*) and two weak peaks (52.58, 52.22) assigned to *tc* (*HH, HT*). The *HH, HT* assignment is made on the basis of the relative peak heights in Figure 2d, recalling that Figure 1d indicates that *HT* > *HH* for *trans* double bonds at high σ_c ; also that *tt* > *tc* even at high σ_c . The C⁴ (*cis*) peaks in the high-*trans* polymer are not listed in Table 6 and occur at 47.34, 47.17 ppm. These are assigned to *ct* (*HH, HT*) on the grounds that *ct* > *cc* when σ_c is low and that the *HH, HT* line order is likely to be the same as for C⁴ *cc* (*HH, HT*) peaks at 47.60, 47.38 ppm: see Table 5. The overlap of C⁴ *cc, HT* (47.38) and C⁴ *ct, HH* (47.34) accounts for the fact that only three rather than four C⁴ (*cis*) peaks are observed in any one spectrum, the peak at 47.17 fading out and that at 47.60 emerging as σ_c increases from 0.11 to 1.0. The line order *tc, tt, cc, ct* is the same for both *HH* and *HT* structures and is identical with that for the corresponding carbon in polynorbornene,² the secondary splitting (0.2 ppm) is also about the same.

C⁷ (*cc*) gives three peaks in the all-*cis* polymer, in the approximate ratio 1:2:1 when made from (\pm)-monomer and with a much stronger central peak when made from (+)-monomer. This can only be explained in terms of triads of which there are four. Their probabilities depend on the

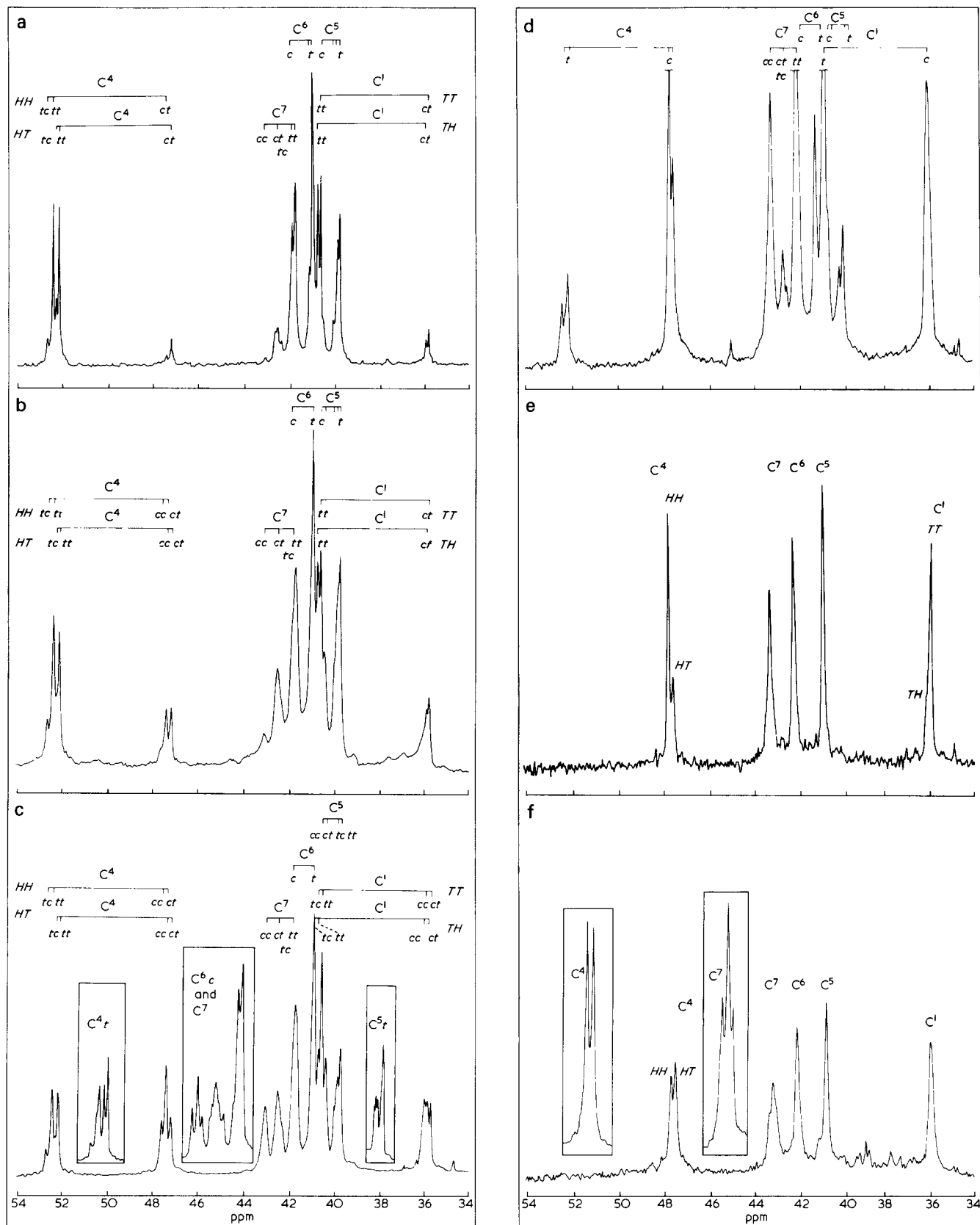
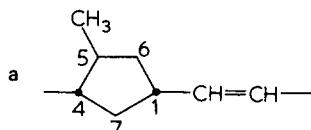


Figure 2 ¹³C n.m.r. spectra (ring-carbon region) of polymers (a)–(f) as in Figure 1. Insets to Figure 2f show fine structure of C⁴ and C⁷ resonances observed at 75 MHz (ppm scale expanded by factor 1.386). Likewise insets to Figure 2c show fine structure of C⁴ (*trans*), C⁷, C⁶ (*cis*) and C⁵ (*trans*) resonances observed at 75 MHz (ppm scale expanded by factor 1.386)

Table 5 Assignment of ring carbons^a in the spectrum of the all-*cis* polymer of (±)-(I)

Position (ppm)	Approximate relative intensity ^b	Coupling ^c	Assignment	Substitution parameters ^d ppm
47.60	50	} CH	<i>cc, HH</i> } C ⁴	β = 8.9 ^e
47.38	50			
43.21 ^f	25	} CH ₂	<i>TT-HH</i> } C ⁷ { <i>TT-HT</i> <i>HT-HT</i> <i>HT-HH</i>	γ + δ = 0.3 ^e
43.02	50			
42.86 ^f	25			
41.99 ^g		CH ₂	C ⁶	β = 8.8 ^e
40.70		CH	C ⁵	α = 7.5
36.03 (36.19) ^h		} CH	<i>cc, TT</i> } C ¹ <i>cc, TH</i>	γ + δ = -2.6 ^e



- a Approximate relative intensity within each group of peaks
 b Number of attached protons as determined by ¹H gated coupling experiment
 c Shift caused at the α, β, γ or δ positions by 5-methyl substitution in polymer of norbornene. For C¹ and C⁷ both directions round the ring have been counted
 d The model compound methylcyclopentane gives β = 8.9, β + δ = -0.7 ppm
 e Only fully resolved at 75 MHz
 f Incipient splitting into two equal lines (*TH/TT*) at 75 MHz
 g Only resolved at 75 MHz when made from (+)-monomer

Table 6 Assignment of ring carbons^{a,b} in the spectrum of the high-*trans* polymer of (±)-(I)

Position (ppm)	Approximate relative intensity ^c	Coupling ^b	Assignment	Substitution parameters ^b
52.58	<i>W</i>	} CH	<i>tc</i> } <i>HH</i> } C ⁴ <i>tt</i> } <i>HT</i>	β = 9.1
52.35	<i>S</i>			
52.22	<i>W</i>			
52.09	<i>S</i>			
41.86 ^d	<i>S</i>	} CH ₂	C ⁷	γ + δ = 0.4
41.73	<i>S</i>			
(41.08)	(<i>W</i>)	} CH ₂	C ⁶	β = 8.7
40.95	<i>S</i>			
40.69	<i>S</i>	} CH	<i>TT, TH</i> } C ¹	γ + δ = -2.5
40.56	<i>S</i>			
39.92	<i>S</i>	} CH	<i>tc</i> } C ⁵	α = 7.4
39.74	<i>S</i>			

- a The minor peaks attributable to ring carbons adjacent to *cis* double bonds are not listed here
 b See footnotes to Table 5
 c Approximate relative intensity: *W* = weak, *S* = strong
 d Only resolved at 75 MHz

fraction *x* of (+)-enantiomer in the monomer. For example the *TT-HH* structure, II, can be formed by successive incorporation of three (+)-enantiomer molecules or three (-)-enantiomer molecules so its probability is $x^3 + (1-x)^3$. The probabilities of the other three structures, *TT-HT*, *HT-HH* and *HT-HT*, are all the same: $(x-x^2)$. The centre peak at 43.02 must clearly be assigned mainly to *TT-HH*, (probability 0.65 when $x = 0.865$) together with one of the other three, most likely *HT-HT* since this differs from *TT-HH* only in the location of the central methyl group. The other

two triads then account for the wing peaks (43.21, 42.86) but cannot be more precisely assigned. The C⁷ (*ct/tc*) peak at 42.5 ppm shows evidence of fine structure at 75 MHz with at least five components. The C⁷ (*tt*) peak in the high-*trans* polymer is only slightly overlapped by the weak C⁶ (*cis*) peak; at 75 MHz it is resolved into two equal peaks presumably corresponding to two pairs of the four triad structures.

No fine structure can be seen for C⁶ (*cis*), nor usually for C⁶ (*trans*), although occasionally in high-*trans* polymers a weak peak or downfield shoulder can be observed at 41.08 ppm (*tc*?).

C⁵ (*cis*) is obscured by C¹ (*trans*) in high-*trans* polymers. No *HH, HT* splitting of C⁵ (*cc*) can be seen in the all-*cis* polymers. In Figure 2c the main C⁵ (*cc*) peak at 40.70 is accompanied by another at 40.48 which is assigned to C⁵ (*ct*). The C⁵ (*trans*) peaks are well resolved at 39.74 (*tt*) and 39.92 (*tc*); further fine structure (*HH, HT, TT*) can be seen in some of the other spectra. The line order for C⁵, namely *cc, ct, tc, tt*, again matches the pattern observed for the corresponding carbon atom in the spectrum of poly-norbornene², with similar splittings.

The C¹ (*cis*) resonance in the all-*cis* polymer made from (+)-monomer, Figure 2e, shows an upfield shoulder which is resolved into a separate peak at 75 MHz. The main peak can therefore be assigned to *cc, TT* and the minor peak or shoulder to *cc, TH*. For polymer of lower *cis* content an upfield shoulder develops (*ct*) which becomes the main resonance when $\sigma_c = 0.25$ and is just resolved into two peaks (*TT, TH*). This matches the behaviour of the C⁴ (*cis*) resonance, with *cc* dominant at high σ_c and *ct* dominant at low σ_c . The C¹ (*trans*) resonance is obscured by C⁵ (*cis*) at high σ_c ; but at low σ_c two equal components (*TT, TH*) are just resolved at 40.69 and 40.56 ppm. The full assignments are indicated in Figure 2.

Methyl carbon

In the all-*cis* polymer made from (+)-monomer the methyl resonance shows a main peak at 18.99 (*HH*) and two weak components at 19.20, 19.12 which indicates partial triad sensitivity, as for C⁷. In the atactic polymers there are two equal peaks, 19.07 and 19.20 ppm.

CONCLUSIONS

The ¹³C n.m.r. spectra of polymers of I can be very satisfactorily interpreted both in broad outline and in fine detail. Information concerning the tacticity of such polymers can be obtained directly from the olefinic part of the spectrum, provided the polymer has been made from resolved monomer of at least 50% optical purity. The problem imposed by the insensitivity of the chemical shifts to tacticity in polynorbornene² can thus be overcome. It has been shown in the present work that the all-*cis* polymer is syndiotactic while polymers having $\sigma_c < 0.55$ are atactic. Substitution shift parameters indicate that the cyclopentane rings are puckered so as to relieve the non-bonded interactions between the *cis*-1,3 olefinic substituents.

ACKNOWLEDGEMENTS

We thank the Science Research Council for financial support. We also thank Miss T. O'Reilly for technical assistance.

REFERENCES

- 1 Ivin, K. J., Eapienis, G. and Rooney, J. J. *J. Chem. Soc. (Chem. Commun.)* 1980, p 1068
- 2 Ivin, K. J., Lavery, D. T. and Rooney, J. J. *Makromol. Chem.* 1977, **178**, 1545
- 3 Berson, J. A. and Ben-Efraim, D. A. *J. Am. Chem. Soc.* 1959, **81**, 4083
- 4 Berson, J. A., Walia, J. S., Remanick, A., Suzuki, S., Reynolds-Warnhoff, P. and Willner, D. *J. Am. Chem. Soc.* 1961, **83**, 3986
- 5 Stothers, J. B. "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972
- 6 Ivin, K. J., Lavery, D. T., Rooney, J. J. and Watt, P. *Rec. Trav. Chim. Pays-Bas* 1977, **96**, M54
- 7 Ivin, K. J., Lavery, D. T., O'Donnell, J. H., Rooney, J. J. and Stewart, C. D. *Makromol. Chem.* 1979, **180**, 1989