

SOME RECENT APPLICATIONS OF ^{13}C NMR SPECTROSCOPY TO THE STUDY OF THE RING-OPENING POLYMERIZATION OF CYCLOALKENES AND RELATED REACTIONS INITIATED BY METATHESIS CATALYSTS

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Abstract - Recent results on the application of ^{13}C n.m.r. spectroscopy in the field of ring-opening polymerization of cycloalkenes, initiated by metathesis catalysts, and the reactions of alkynes initiated by the same catalysts, are reviewed and extended, especially in relation to the polymerization of 5,5-disubstituted derivatives of bicyclo[2.2.1]hept-2-ene. Direct and indirect observations of the tacticity with respect to both *cis* and *trans* double bonds in these polymers is reported. Applications to the detection of end groups, *cis/trans* isomerization of double bonds in the polymer chain, and double bond migration are also reviewed.

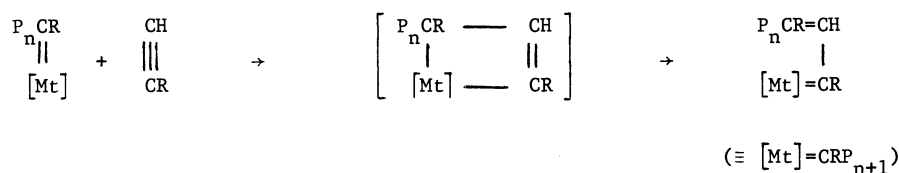
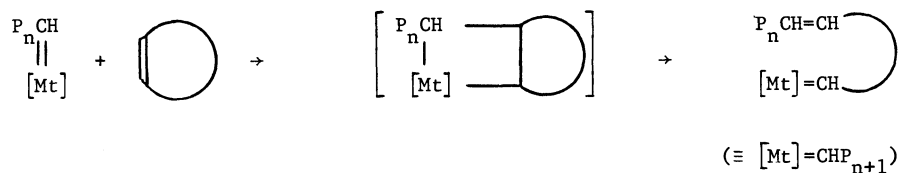
INTRODUCTION

The ring-opening polymerization of cycloalkenes is a particular case of the olefin metathesis reaction. Such reactions are initiated by a variety of catalyst systems, generally based on a compound of one of the following transition metals: Ti, V, Nb, Ta, Mo, W, Re, Ru, Os, Ir. It is generally desirable, though not always essential, to use a co-catalyst; typical combinations include $\text{WCl}_6/\text{EtAlCl}_2$, $\text{MoCl}_5/\text{R}_4\text{Sn}$ ($\text{R} = \text{Me, Bu, Ph}$), and $\text{TiCl}_4/\text{LiAlR}_4$.

It was proved many years ago by isotopic labelling (^2H or ^{14}C), that the double bond itself is broken during the metathesis reaction of both acyclic (Ref. 1 & 2) and cyclic olefins (Ref. 3). More recently it has been shown that the same or similar catalyst systems can induce two types of reaction in alkynes, namely metathesis itself, again demonstrated (Ref. 4) by isotopic labelling (^{13}C), and polymerization (Ref. 5). That the mechanisms of the reactions of alkenes and alkynes induced by these catalysts are intimately connected is shown by the fact that small amounts of alkynes sometimes act as cocatalysts for the reactions of cycloalkenes (Ref. 6).

There is now a considerable body of evidence to show that olefin metathesis reactions (and possibly also the above polymerization reactions of alkynes) are propagated by a metallacarbene generated from the catalyst system, sometimes with the assistance of the substrate (Ref. 7). The relatively stable metallacarbenes $\text{Ph}_2\text{C}=\text{W}(\text{CO})_5$ and $\text{Ph}(\text{MeO})\text{C}=\text{W}(\text{CO})_5$ can also be used as initiators of ring-opening polymerization of cycloalkenes, but sometimes need an acetylenic cocatalyst (Ref. 6).

The propagation reactions, as represented below for the polymerization of cycloalkenes and alkynes, are thought to involve metallacyclobutane and metallacyclobutene intermediates respectively, though it must be said that there is no direct spectroscopic evidence either for these intermediates or for the metallacarbenes. $[\text{Mt}]$ denotes the transition metal surrounded by various permanent ligands.



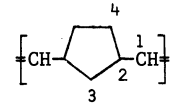
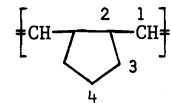
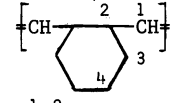
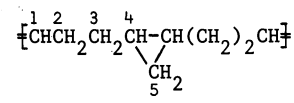
There are many aspects of the structure of these polymers which can be elucidated by ^{13}C n.m.r. spectroscopy. Not only can the basic structure be verified and the proportion of cis double bonds (σ_c) determined, but it is possible to estimate the proportions of various types of pair sequence from the fine structure, provided the number of carbon atoms in the main chain of the repeating unit is not too large (not more than 7). This in turn provides information about the mechanism. Thus one can determine (a) the proportions of double bond pair sequences, represented as cc, ct, tc, tt (Ref. 8), (b) the proportions of m and r dyads when there are chiral centres in the chain (Ref. 9), (c) the proportions of head-head (HH), head-tail (HT) and tail-tail (TT) structures in polymers made from unsymmetrically substituted cycloalkenes (Ref. 9), and (d) the proportions of compositional dyads M_1M_1 , M_1M_2 , and M_2M_2 in ring-opened copolymers of two cycloalkenes M_1 and M_2 (Ref. 10). It is also possible to detect end groups by ^{13}C n.m.r. spectroscopy when the polymers are of sufficiently low molecular weight (less than 5000) (Ref. 11) and to observe defect structures or other products resulting from secondary (Ref. 12) or concurrent reactions (Ref. 13).

Here we shall gather together some examples of these applications of ^{13}C n.m.r. spectroscopy from the recent literature and also present some new data; also see references (14) and (15). The ^{13}C n.m.r. spectra were obtained at 22.63 MHz in CDCl_3 as solvent, with internal TMS as reference, unless otherwise stated.

BASIC STRUCTURE OF POLYMERS

Some recently published examples of the ^{13}C chemical shifts of polymers of cycloalkenes formed using metathesis catalysts are shown in Table 1. The spectra are entirely consistent with the structure corresponding to ring-opening at the double bond.

TABLE 1. ^{13}C chemical shifts for some ring-opened polymers of bicycloalkenes and related polymers^a

Polymer	cis				trans				Ref.
	C ¹	C ²	C ³	C ⁴	C ¹	C ²	C ³	C ⁴	
1 	133.88	38.70	42.77	33.32	133.10	43.15	41.40	32.30	(16)
2 	130.9	42.16	32.5	23.30	131.2	47.46	31.5	23.30	(17)
3 	130.9	37.8	30.3	23.6	132.4	43.5	30.3	23.6	(18)
4 $\text{[CHCH}_2\text{CH}_2\text{CH]}_n$	129.66	27.52			130.11	32.84			(19)
5 	129.72	27.66	28.88	15.52	130.20	33.06	28.88	15.52	(20)
		(C ⁵ 10.91)				(C ⁵ 10.91)			
6 $\text{[CHCH}_2\text{CH}_2\text{CH}_2\text{(CH}_2\text{)}_3\text{CH]}_n$	129.98	27.36	29.87	29.35	130.46	32.71	29.74	29.18	(21)

^aIn most cases the spectra of polymers containing both cis and trans double bonds show additional fine structure (cc,ct;tt,tc); for details see the original papers

^bSee Fig. 1

The following may be noted.

- (1) The cis olefinic carbons generally appear upfield from the trans olefinic carbons except in the case of the polymers of norbornene (1) and its derivatives (Ref. 9 and 22).

- (2) The carbons α to a cis double bond always appear about 5 ppm upfield from carbons α to a trans double bond, as found in simple olefins.
- (3) C^4 in 2 (23.3 ppm) is substantially upfield from the corresponding carbon (C^3) in 1 (41.4 - 42.8 ppm) as a result of the replacement of two β substituents by two γ substituents. The spectrum of a sample of 2 is shown in Fig. 1.

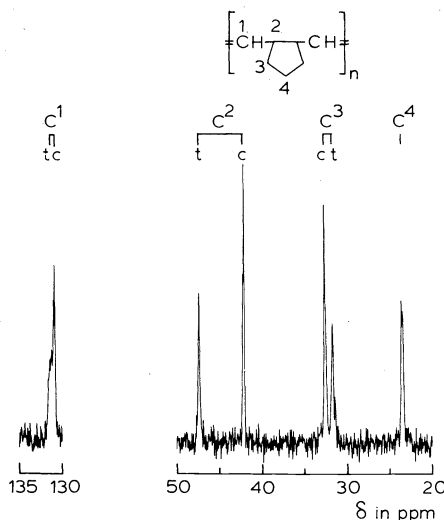


Fig. 1. ^{13}C n.m.r. spectrum of polymer 2 (Table 1) made from bicyclo[3.2.0]hept-6-ene using $\text{WCl}_6/\text{EtAlCl}_2/\text{EtOH}$ (1/4/1) as catalyst; $\sigma_c = 0.62$. The olefinic carbons give a total of eight lines [possibly (tt,tc,ct,cc) $\times$ (m,r)]

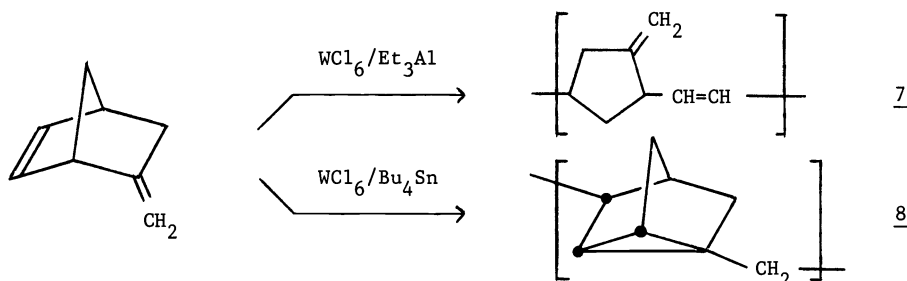
- (4) In going from 4 to 3 or 2 the C^1 and C^2 resonances move downfield, as expected.

In the ring-opening polymerization of cis,cis-cycloocta-1,5-diene to give 4, only one of the two double bonds in the monomer is initially involved so that in the polymer, alternate double bonds have cis structure. This is shown by the absence of the C^1 (tt) peak at 130.11 ppm in the initially formed polymer, olefinic peaks being seen only at 130.24 (tc), 129.68 (cc) and 129.55 ppm (ct). The rate of cis/trans isomerization of double bonds in the polymer chain, leading to the appearance of the tt peak, depends very much on the catalyst system. Catalysts of the type $\text{WCl}_6/\text{R}_4\text{Sn}$ ($\text{R} = \text{Ph}, \text{Me}, \text{allyl}$) give a high σ_c and no sign of cis/trans isomerization even after several hours. With $\text{WCl}_6/\text{EtAlCl}_2$ (1/4) polymerization proceeds to 34% conversion in 40s ($\sigma_c = 0.8$) with no sign of the tt peak; but if the catalyst components are mixed in the ratio 1/10 ($\text{WCl}_6/\text{EtAlCl}_2$) before adding the monomer (solvent PhCl), the polymerization goes to 80% conversion in 5s ($\sigma_c = 0.6$) and substantial cis/trans isomerization has already occurred ($\text{tt} \approx \text{tc}$ and $\text{cc} \approx \text{ct}$). The rate of cis/trans isomerization is evidently very sensitive to the nature of the catalyst; it may proceed by a metathesis mechanism, though this is not the only possibility.

When the ratio $\text{EtAlCl}_2/\text{WCl}_6$ exceeds 10 another type of secondary reaction is observed, namely migration of the double bonds along the chain (Ref. 12). Thus when the ratio is 20, the polymerization of cis,cis-cycloocta-1,5-diene gives a polymer whose spectrum contains not only the usual peaks corresponding to $n = 2$ in $[-\text{CH}(\text{CH}_2)_n\text{CH}-]$ but also peaks characteristic of the polymer of cyclopentene ($n = 3$) and another set of peaks attributed to the unit with $n = 1$. Likewise, starting from cyclopentene one can observe isomerization to give structures corresponding to $n = 2$ and 4 as well as $n = 3$ (Ref. 12). Such reactions are catalyzed by the presence of the excess EtAlCl_2 .

An example of a concurrent as distinct from consecutive side reaction is found in the polymerization of 5-methylenebicyclo[2.2.1]hept-2-ene (Ref. 13). When polymerized by $\text{WCl}_6/\text{Et}_3\text{Al}$ it yields the expected ring-opened polymer 7, characterized by olefinic carbons at 154.92, 154.66 ppm ($=\text{C}$), 106.24 ppm ($=\text{CH}_2$) and two groups of four peaks in the region 131 - 135 ppm, corresponding to TH, TT, HH, HT carbons in cis and trans double bonds.

However, when $\text{WCl}_6/\text{Bu}_4\text{Sn}$ is used as catalyst the polymer is totally devoid of double bonds and has a ^{13}C n.m.r. spectrum consistent with 8. The formation of this polymer is known to proceed through a cationic mechanism (Ref. 23) and it is evident that the reaction must be extremely sensitive to traces of cationic species in metathesis catalyst systems. Other catalyst systems give a mixture of the two types of polymer and the formation of 8 can be



suppressed to some extent by addition of tertiary amines in controlled amount. A further point of interest is that the signals due to the three marked carbons in 8 show a splitting into two equal lines. This is attributed to the fact that the monomer consists of equal proportions of two enantiomers so that if these enter the chains at random there will be equal proportions of m and r dyad structures. As we shall see below the same type of effect can sometimes be seen in the ring-opened polymers of norbornene derivatives.

DETECTION OF END GROUPS

When the ring-opening polymerization of cycloalkenes is conducted in the presence of acyclic olefins the latter act as chain transfer agents, and by the use of sufficient transfer agent the molecular weights can be reduced to the point where the end groups derived from the chain transfer agent by cleavage of the double bond are readily detectable by ^{13}C n.m.r. spectroscopy. Even if the main product is of too high a molecular weight it is sometimes possible to separate out the shorter chains by fractionation in order to examine the end groups.

Systems in which we have identified end groups formed in this way by chain transfer are summarized in Table 2. The line positions characteristic of each end group are given in Table 3. Two of the relevant spectra are shown in Figs. 2 and 3; (Ref. 24). These results fully support the established fact that the metathesis reaction involves cleavage of the double bond.

TABLE 2. End groups detected by ^{13}C n.m.r. in polymers of ring-opened cycloalkenes prepared in the presence of acyclic olefins as chain transfer agents. For line positions characterizing the end groups see Table 3.

Reacting system ^a	Structure of polymer
CPE/1-C ₅	$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}[\text{CH}(\text{CH}_2)_3\text{CH}]_n\text{CH}(\text{CH}_2)_2\text{CH}_3$
NBE/1-C ₆	$\text{CH}_2=\text{CH}-\text{Cyclopentene}-\text{CH}[\text{CH}-\text{Cyclopentene}-\text{CH}]_n\text{CH}-\text{Cyclopentene}-\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$
NBE/1,7-C ₈	$\text{CH}_2=\text{CH}-\text{Cyclopentene}-\text{CH}[\text{CH}-\text{Cyclopentene}-\text{CH}]_n\text{CH}-\text{Cyclopentene}-\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}_2$
NBE/STY	$\text{CH}_2=\text{CH}-\text{Cyclopentene}-\text{CH}[\text{CH}-\text{Cyclopentene}-\text{CH}]_n\text{CH}-\text{Cyclopentene}-\text{CH}=\text{CHPh}$
NBDE/1-C ₆	$\text{CH}_2=\text{CH}-\text{Cyclopentene}-\text{CH}[\text{CH}-\text{Cyclopentene}-\text{CH}]_n\text{CH}-\text{Cyclopentene}-\text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$

^aCPE = cyclopentene, NBE = norbornene, NBDE = norbornadiene, 1-C₅ = pent-1-ene, 1-C₆ = hex-1-ene, 1,7-C₈ = octa-1,7-diene, STY = styrene.

TABLE 3. ¹³C chemical shifts^a in ppm characterizing the end groups of the polymers shown in Table 2.

$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH} \\ \\ (\text{CH}_2)_4 \\ \\ \text{CH} \\ \\ \text{CH} \\ \\ \text{Cyclopentyl} \\ \\ \text{CH} \\ \end{array}$	$\begin{array}{c} 114.23 \\ \\ 139.00 \\ \\ \\ \{128.68 \\ 128.42\} \\ \{135.24 \\ 135.16 \\ 134.98 \\ 134.90\} \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH} \\ \end{array}$	$\begin{array}{c} 114.44 \\ \\ 138.74 \\ \\ 33.27 \\ \\ 28.91 \\ \\ \\ \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH} \\ \\ \text{Cyclopentyl} \\ \\ \text{CH} \\ \end{array}$	$\begin{array}{c} \{112.33 \\ 112.20\} \\ \{143.48 \\ 143.31\} \\ \{44.53 \\ 44.27\} \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH} \\ \\ \text{Cyclopentyl} \\ \\ \text{CH} \\ \end{array}$	$\begin{array}{c} \{113.28 \\ 113.15\} \\ \{142.62 \\ 142.54\} \\ 49.84 \end{array}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH} \\ \\ \text{CH} \\ \\ (\text{CH}_2)_3 \\ \end{array}$	$\begin{array}{c} 13.68 \\ \\ 22.79 \\ \\ 34.78(t) \\ \\ \\ \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH} \\ \\ \text{CH} \\ \end{array}$	$\begin{array}{c} 13.98 \\ \\ \{22.31 \\ 22.18\} \\ \{32.19 \\ 31.76\} \\ \{32.11(t) \\ 27.23(c)\} \\ \{128.73 \\ 128.60\} \\ 135.03 \end{array}$	$\begin{array}{c} \text{Ph} \\ \\ \text{CH} \\ \\ \text{CH} \\ \\ \text{Cyclopentyl} \\ \end{array}$	$\begin{array}{c} \{128.47, 128.12, 127.91, 127.52, \\ 127.44, 126.74, 125.92\} \\ 138.24, 138.05, 137.92 \end{array}$		

^aThe fine structure is to be attributed to *cis/trans* isomerism about the adjacent double bonds. The chemical shifts for the repeating units may be found in the literature (Ref. 11, 16 and 25).

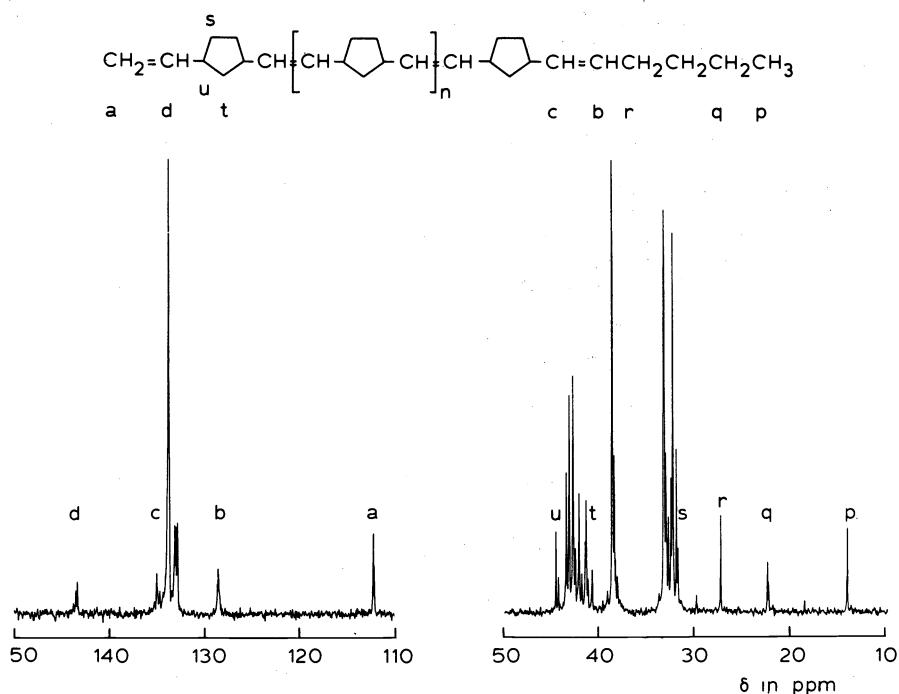


Fig. 2. ^{13}C n.m.r. spectrum of polymer made from 1 g norbornene in the presence of 5 ml hex-1-ene in 10 ml benzene. Catalyst: 25 mg $\text{W}(\text{CO})_3\text{Cl}_2(\text{AsPh}_3)_2$. Mixture refluxed for 1 h. Spectrum is that of the second fraction.

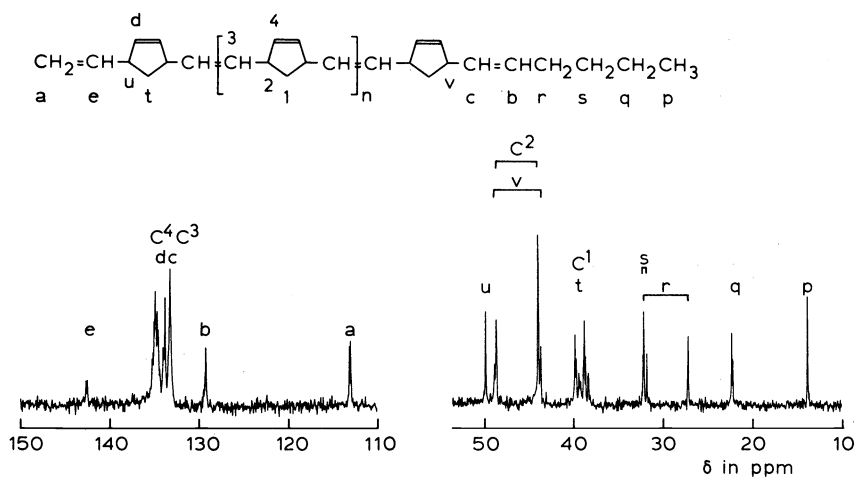
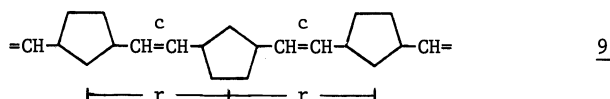


Fig. 3. ^{13}C n.m.r. spectrum of polymer made from 2 ml norbornadiene in the presence of 10 ml hex-1-ene in 20 ml benzene. Catalyst: 25 mg $\text{W}(\text{CO})_3\text{Cl}_2(\text{AsPh}_3)_2$. Mixture refluxed for 20 min. Spectrum is that of the sixth fraction. (First fraction gives a spectrum with undetectable end groups).

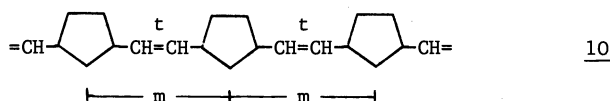
The detection of end groups in polymers made from cycloalkenes in the absence of chain transfer agents would, of course, provide valuable information concerning the nature of the initiating metallocarbene, as well as the termination process, but so far has not been achieved by ^{13}C n.m.r. However, it seems quite possible that the necessary sensitivity could be attained by fractionation of the product to obtain the low molecular weight components. This would provide evidence to parallel that obtained from the first-formed products in the metathesis reactions of acyclic olefins (Ref. 26 and 27).

DIRECT OBSERVATION OF TACTICITY IN POLYMERS OF NORBORNENE DERIVATIVES

On the assumption that ring-opening polymerization of cycloalkenes is propagated by metallocarbenes which may have either a left-handed (P_L) or right-handed (P_R) configuration, it may be predicted that, provided P_L and P_R do not racemize between successive additions of monomer (or relax into a symmetrical form P_S), then an all-cis polymer made from norbornene or one of its derivatives should have a syndiotactic ring sequence,



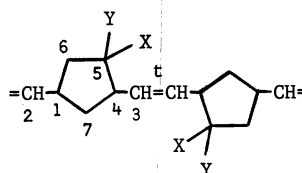
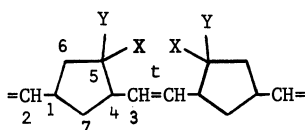
whereas an all-trans polymer should have an isotactic ring sequence (Ref. 16).



When both cis and trans double bonds are formed, a cis double bond will be associated with an r dyad and a trans double bond with an m dyad, again provided the identities of P_L and P_R are not lost before each addition of monomer. If, however, there is partial racemization of P_L and P_R between successive monomer additions (or relaxation to P_S), then it may be predicted that $r > m$ for cis double bonds and $m > r$ for trans double bonds, r and m being equal when there is total racemization or relaxation.

Previously we had been unable to observe this m/r effect directly in the ^{13}C n.m.r. spectra of polymers made from norbornene (Ref. 16) or its racemic exo-5-methyl (Ref. 9) or endo-5-methyl (Ref. 22) derivatives and had to resort to the use of optically active monomer in order to transform the unobservable tacticity effect into an observable TH,TT,HH,HT splitting of the olefinic carbon resonance (Ref. 9). A syndiotactic polymer then has an HH,TT structure while an isotactic polymer has an all-HT structure, when made from an optically pure enantiomer.

Recently we have found (Ref. 28) that when there are two substituents ($X = \text{exo}$, $Y = \text{endo}$) in the 5-position the C^3 (HH) and C^4 (HH) resonances in the all-trans polymer made from racemic monomer sometimes show a splitting which can be attributed to structures 11 and 12, differing only in their tacticity, m and r .



11 (HH,m)

12 (HH,r)

For example, the olefinic region of the spectrum of the polymer for which $X = Y = \text{CH}_3$ is shown in Fig. 4.

When the polymer is made from monomer of high optical purity only one HH line is seen (Fig. 4a), corresponding to dyad structure 12, but when made from racemic monomer, two HH lines are seen (Fig. 4b), since now it is possible for the dyad structure 11 to be formed by successive enchainment of the two mirror-image forms. The m/r ratio may be derived from both spectra in Fig. 4: directly from the ratio of the two HH peak intensities in Fig. 4b; and indirectly from the ratio of the HT ($\equiv m$) and HH ($\equiv r$) peak intensities in Fig. 4a, with a small correction for the presence of 8.5% of the minor enantiomer. In each case a value of $m/r = 1.3$ is obtained, consistent with substantial but not total racemization or

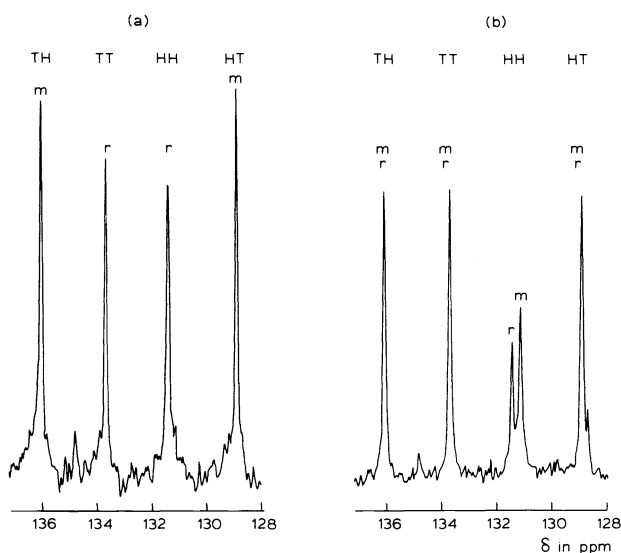


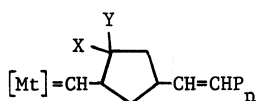
Fig. 4. ^{13}C n.m.r. spectrum (olefinic region) of all-*trans* polymer made from (a) (+)- and (b) (±)-5,5-dimethylbicyclo[2.2.1]hept-2-ene. Catalyst: $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in EtOH/PhCl (1/1) at 75°C . Optical purity of (+)-monomer = 83%.

relaxation of the intermediate P_ℓ and P_r metallacarbenes before each addition of monomer.

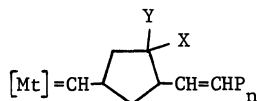
The fact that for the olefinic carbons *m,r* splitting is seen only in the HH *trans* resonance is understandable since it is in the HH structure that the conformational populations about the two bonds attaching the olefinic carbons to the rings are most likely to be sensitive to the *m* or *r* relationship of the two rings. It is not possible to say whether the same type of *m,r* splitting occurs with *cis* double bonds since all-*cis* polymers are highly syndiotactic, and with polymers of intermediate *cis* content the HH *cis* and HH *trans* peaks are not well resolved.

Other polymers where we have observed splitting in the HH *trans* resonance are listed in Table 4. Usually it is necessary to have two substituents present but occasionally the effect is observed when there is a single endo substituent (COOR). It will be seen that in some cases the relative intensity of the two lines is reversed compared with that in the case $\text{X} = \text{Y} = \text{CH}_3$. This suggests that the line order is also reversed in these cases. The relative magnitude of the C^3 *m* and *r* lines can vary substantially with the catalyst and there are often parallel changes in the C^4 (*trans*) fine structure. This is found not only with the polymer having $\text{X} = \text{Y} = \text{CH}_3$ but also in other cases such as that shown in Fig. 5 ($\text{X} = \text{CH}_3$, $\text{Y} = \text{COOCH}_3$). These effects presumably reflect different degrees of racemization or relaxation of P_ℓ and P_r between successive monomer additions. Fig. 5b seems to indicate a remarkably high degree of tacticity in a high *trans* polymer.

It should be noted that in the polymerization of substituted norbornenes there are two types of propagating species, represented by 13 and 14.



13



14

TABLE 4. Polymers^a of norbornene derivatives showing a splitting of the trans HH olefinic resonance in the ¹³C n.m.r. spectrum. X = exo-5-substituent, Y = endo-5-substituent.

X	Y	HH line positions ppm		Splitting ppm	Relative intensities (upfield/downfield)
CH ₃	CH ₃	131.43	131.14 ^b	0.29	1.3
CH ₃	CH ₂ OH	130.58	129.98	0.60	2
CH ₂ OH	CH ₃	131.10	130.80	0.30	c
CH ₃	COOH	131.32	131.02	0.30	1.0, 0.47 ^d
COOH	CH ₃	130.70	130.56	0.14	e
H	COOCH ₃	131.36	130.97	0.39	0.8
H	COOC ₂ H ₅	131.61	131.02	0.59	
CH ₃	COOCH ₃	131.01 ^e			
CH ₃	COOC ₂ H ₅	131.29	130.96	0.33	1.1
COOCH ₃	CH ₃	130.82	130.63	0.19	1.0

^aEssentially all-trans, made using RuCl₃·3H₂O in EtOH/PhCl (1/1) at 50 - 70°C as catalyst unless otherwise indicated.

^bUpfield peak assigned to m dyad in this case; see Fig. 4.

^cIrCl₃ catalyst, σ_c = 0.2; intensities obscured by overlap of cis peak.

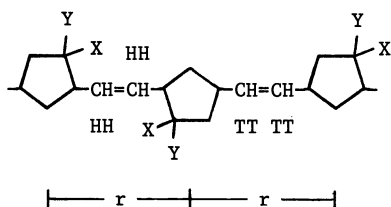
^dOsCl₃ catalyst (all-trans); note variation of tacticity with catalyst.

^eBroadened but not resolved; see Fig. 5a.

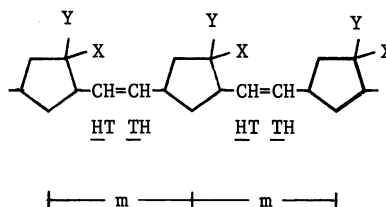
13 can add monomer to give HH or HT structures while 14 can add monomer to give TH or TT structures. If the two species racemize or relax to P_S at different rates, then in principle it is possible for the m/r ratios for HH, HT and TT structures to be different when the polymer is made from racemic monomer.

INDIRECT OBSERVATION OF TACTICITY IN POLYMERS OF NORBORNENE DERIVATIVES

This method depends on the fact that a syndiotactic polymer made from a single enantiomer of a 5-substituted norbornene derivative has a HH,TT structure 15, while an isotactic polymer must have an all-HT structure 16.



15



16

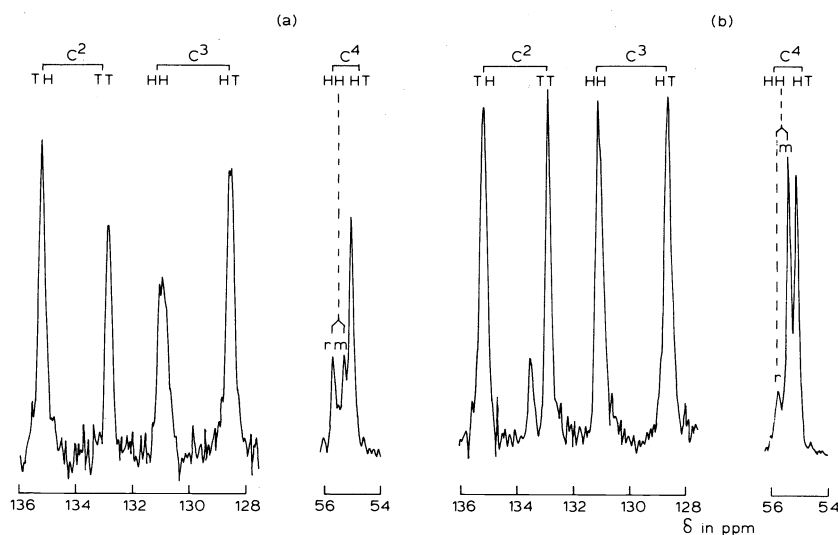


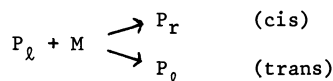
Fig. 5. ^{13}C n.m.r. spectra ($\text{C}^2, \text{C}^3, \text{C}^4$ regions, see 11) for all-trans polymers with $\text{X} = \text{CH}_3$, $\text{Y} = \text{COOCH}_3$. (a) Using $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in MeOH/PhCl (1/1) as catalyst at 60°C ; (b) using RuCl_3 -cyclooctadiene complex in EtOH/PhCl (1/1) as catalyst at 53°C (N.B. The behaviour of this complex is somewhat variable and dependent on its mode of preparation and storage; another sample gave a result similar to (a)). The assignments to m and r are based on the prediction that $m > r$ in an all-trans tactic polymer.

An atactic polymer will have equal proportions of carbons of the types defined as TH, TT, HH, HT in 15 and 16. Furthermore the chemical shifts can be expected to lie in this order (downfield to upfield), with a set of four lines for cis double bonds and another set of four lines for trans double bonds. The application of this method has already been illustrated in Fig. 4a.

The method was originally applied to the monomer with $\text{X} = \text{CH}_3$, $\text{Y} = \text{H}$ and it was demonstrated that the all-cis polymer was highly syndiotactic (ReCl_5 catalyst), while high-trans polymers ($\sigma_c = 0.1 - 0.3$) were essentially atactic (Ref. 9). An important prediction of the theory, if only racemization of P_l and P_r are involved (and no other type of propagating species), is that in high-cis polymers the fraction of m dyads, σ_m , for trans double bonds should be the same as the fraction of r dyads, σ_r , for cis double bonds. Unfortunately it is difficult to test this prediction with polymers made from the monomer with $\text{X} = \text{CH}_3$, $\text{Y} = \text{H}$ because of overlap of the cis and trans olefinic ^{13}C peaks. This difficulty can be overcome by using instead the monomer with $\text{X} = \text{Y} = \text{CH}_3$. Not only are the olefinic peaks in the ^{13}C n.m.r. spectrum of this polymer spread over a wider range but the monomer can also be obtained more readily in high optical purity (Ref. 28).

The results using the monomer with $\text{X} = \text{Y} = \text{CH}_3$ confirm the very high syndiotacticity of the all-cis polymer, made using ReCl_5 as catalyst. They also show that the all-trans polymer, made using RuCl_3 as catalyst, has a small degree of isotacticity ($\sigma_m = 0.57$); see Fig. 4. However, most important of all, it is found that in the intermediate cases ($\sigma_c = 0.2 - 0.8$), σ_m for trans double bonds is generally the same as σ_r for cis double bonds, within the experimental error, supporting the idea that the tacticity is governed in these cases by the

extent of racemization of P_L and P_R before each monomer addition. An example is shown in Fig. 6, where there is a high retention of tacticity even at $\sigma_c = 0.61$. A similar result was obtained when the polymerization was initiated by $\text{Ph}(\text{MeO})\text{C}=\text{W}(\text{CO})_5/\text{PhC}\equiv\text{CH}$ ($\sigma_c = 0.47$). With $\text{WCl}_6/\text{Me}_4\text{Sn}$ (1/2) as catalyst the tacticity is relatively low, with $(\sigma_m)_t = 0.59 \pm 0.04$, $(\sigma_r)_c = 0.66 \pm 0.04$, even though the *cis* content is quite high ($\sigma_c = 0.69$). With $\text{MoCl}_5/\text{Et}_3\text{Al}$ as catalyst there is a similar loss of tacticity, with $(\sigma_m)_t = 0.71 \pm 0.04$ and $(\sigma_r)_c = 0.64 \pm 0.03$, but the *cis* content in this case is much lower ($\sigma_c = 0.29$). Thus the tacticity does not correlate with the *cis* content, the latter being controlled by the relative rates of addition of monomer M in the two modes,



while the tacticity is controlled by the rate of attainment of the equilibrium

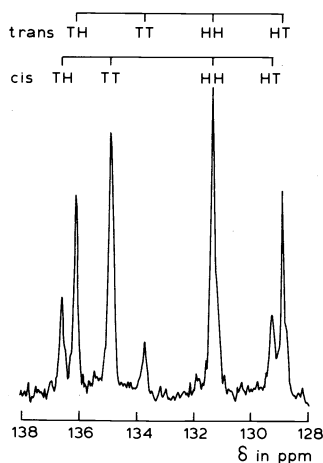
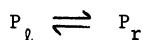
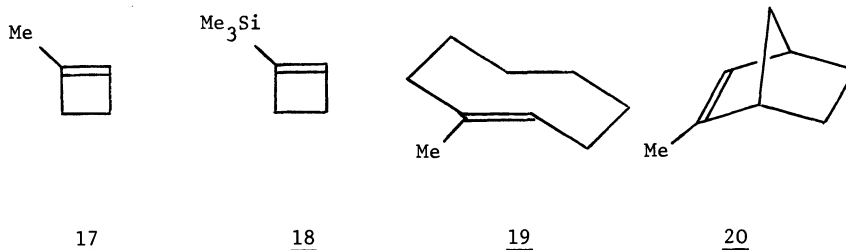


Fig. 6. ^{13}C n.m.r. spectrum (olefinic region) of a ring-opened polymer ($\sigma_c = 0.63$) of (-)-5,5-dimethylbicyclo[2.2.1]hept-2-ene made using $\text{WCl}_6/\text{Bu}_4\text{Sn}$ (1/2) as catalyst. Optical purity of monomer = 74%. After correction for the presence of 13% (+) enantiomer the TT/TH ratios give $(\sigma_m)_t = 1.04 \pm 0.06$, $(\sigma_r)_c = 1.00 \pm 0.10$.

However, it should be mentioned that in three cases out of twelve the values of $(\sigma_m)_t$ and $(\sigma_r)_c$ differ by more than the experimental error. For example with RuCl_3/COD complex as catalyst one result gave $(\sigma_m)_t = 0.77 \pm 0.04$, $(\sigma_r)_c = 0.90 \pm 0.04$, with $\sigma_c = 0.65$. Such exceptions can only be interpreted in terms of at least two propagating species with different kinetic parameters (P_L and P_R counting as one species). There are a number of possibilities so far as additional species are concerned (e.g. the symmetrical metallocarbene P_S could be involved); and there are several ways in which they could be formed (e.g. direct from the catalyst; by relaxation of P_L and P_R ; or by direct formation from the intermediate metallacyclobutane). These possibilities will be discussed in detail elsewhere.

TENDENCY TO HEAD-TAIL ADDITION

It has been shown (Ref. 29, 30 and 31) that there is a very strong tendency towards head-tail addition in the ring-opening polymerization of the cycloalkenes 17, 18, 19, 20, all of which are substituted at the double bond. The proportions of cis double bonds formed using $\text{Ph}_2\text{C}=\text{W}(\text{CO})_5$ as catalyst



are 87% (Ref. 29), 100% (Ref. 30), 24% (Ref. 31) and about 40% (Ref. 30), respectively. The evidence for predominant head-tail structures comes directly from ^{13}C n.m.r. spectra and only in the case of 17 is a small amount (10%) of HH and TT structure detected. It is interesting to note that if it were possible to produce an all-cis, all-HT, syndiotactic polymer from a racemic sample of 20 it would be obliged to consist of an alternating copolymer of the two enantiomers, and by implication it would be more difficult to polymerize the pure enantiomers with the same catalyst.

It is clear that with monomers 17 to 20 the substituent at the double bond will interact strongly with the propagating metallacarbene and direct the course of the propagation reaction so far as the position of the substituent is concerned, regardless of whether cis or trans double bonds are being formed. For racemic norbornene derivatives with substituents in the 5-position we generally find that the polymer contains equal proportions of TH, TT, HH, HT structures. However, occasionally one finds a small bias towards HT addition. An example is shown in Fig. 7 where $\text{HT}/\text{HH} = 1.6$. The effect is most noticeable

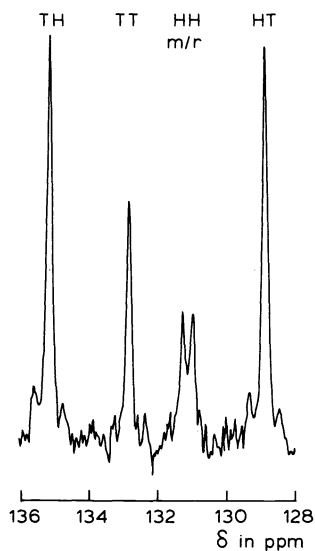
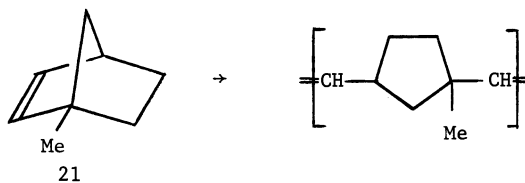


Fig. 7. ^{13}C n.m.r. spectrum (olefinic region) of a ring-opened polymer made from the monomer with $\text{X} = \text{CH}_3$, $\text{Y} = \text{COOH}$ (cf. Table 4). Catalyst: $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in EtOH at 60°C . N.m.r. solvent $\text{DMSO}-d_6/80^\circ\text{C}$.

when the endo substituent is either COOH or COOR suggesting that the directing influence involves the interaction of this group with the reactive site, though the mechanism of this interaction is not clear.

We have also succeeded in polymerizing 1-methylbicyclo[2.2.1]hept-2-ene **21** to give both an all-*trans* polymer, using RuCl₃·3H₂O in EtOH/PhCl at 70°C as catalyst, and a high-*cis* polymer ($\sigma_c = 0.69$), using WCl₆/Me₄Sn at 20°C as catalyst.



The ¹³C n.m.r. spectrum of the all-*trans* polymer shows four olefinic peaks at 138.94 (HT), 135.65 (HH), 133.25 (TT), 130.08 ppm (TH) without any significant bias in favour of the HT structure. In the spectrum of the high-*cis* polymer there are *cis*-olefinic carbon resonances in the regions 139.1 and 134.8 ppm, each with fine structure, but it is not yet clear whether these represent accidental coincidences of two pairs of lines or are a genuine indication of a preferred mode of addition (either HH, TT, or all-HT). (Ref. 31).

CONCLUSIONS

¹³C n.m.r. spectroscopy finds many applications in the chemistry of ring-opening polymerization of cycloalkenes initiated by metathesis catalysts. Not only can the basic structure of the polymers be verified but various types of pair sequence (double bonds, chiral centres, copolymer units) can be detected and quantitatively determined. In polymers of norbornene derivatives the tacticity can sometimes be observed from the fine structure of the olefinic resonance in the head-head structure. A more general method of determining tacticity involves the use of optically active monomers, thereby transforming the tacticity effect into a more readily detectable head-head, tail-tail or head-tail effect. End groups can also be detected by ¹³C n.m.r. in these polymers when an acyclic olefin has been used as chain transfer agent. Secondary reactions, such as *cis/trans* isomerization of the double bonds in the polymer chain, or double bond migration are also readily observed.

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