

The determination and interpretation of tacticity in ring-opening metathesis polymerization

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The microstructure of ring-opened metathesis polymers formed from cyclic olefins may be defined in terms of tacticity as well as the distribution and ratio of *cis/trans* double bonds; the current availability of a wide range of catalyst systems allows almost infinite variation of these microstructural features. A methodology is described whereby the tacticity of polymers formed from bicyclo[2.2.1]heptene (norbornene) and derivatives, using these catalysts, may be determined by ^{13}C and ^1H n.m.r. spectroscopic techniques. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The stereoregularity of polymer molecules is a microstructural feature of great importance which determines, to a large extent, the bulk properties and hence the commercial value of many polymeric materials. The seminal work in this field was carried out in the 1950s and was centred on Ziegler's metal-catalysed polymerization of α -olefins and the recognition by Natta of the relationship between tacticity, a term first used by Natta to describe stereoregularity, and physical properties. Since then, substantial research effort in polymer chemistry has been devoted both to the determination of tacticity and to the development of reaction systems which promote the formation of stereoregular polymers¹.

Although the original microstructure determinations were carried out on polymers in the solid state using the techniques of X-ray crystallography, the application of high-field n.m.r. spectroscopy meant that polymers could be studied more conveniently in solution where their tacticity in terms of dyad, triad structures etc. could be determined². The combination of such analytical techniques and the advent of the new homogeneous metallocene catalysts has meant that polymers with a complete range of microstructures can now be prepared and studied^{3,4}.

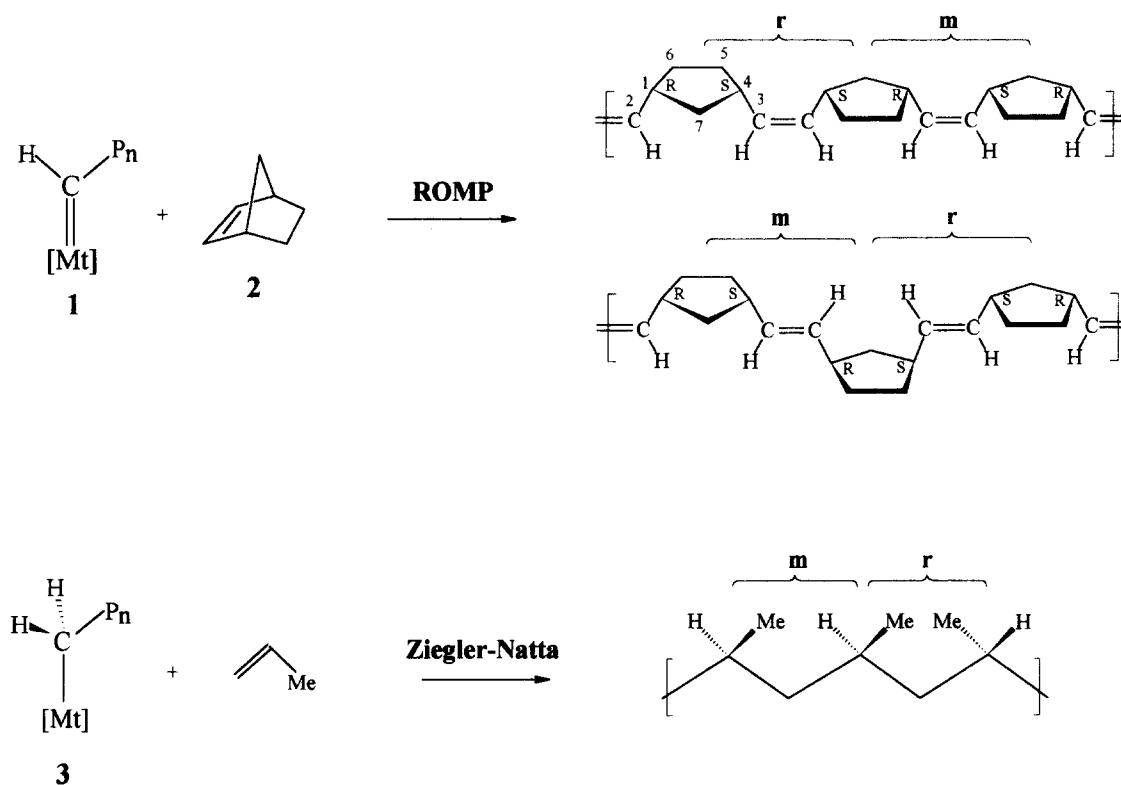
Mechanistically related to these α -olefin polymerizations is the ring-opening metathesis polymerization (ROMP) of cyclic olefins which, by way of contrast, yields elastomers where the double bond, which has variable stereochemistry, is retained in the product, a consequence of propagation via a metal carbene, **1**, rather than a metal alkyl species, **3** (Scheme 1). ROMP polymers are therefore microstructurally more complex and one has to consider possible variations in double bond stereochemistry, as well as tacticity, in the analysis of microstructure^{5,6}.

Although a number of metathesis polymerizations are still carried out using 'classical' catalyst systems derived from transition metal halides^{7–15}, ROMP is enjoying something of a renaissance due to the development of

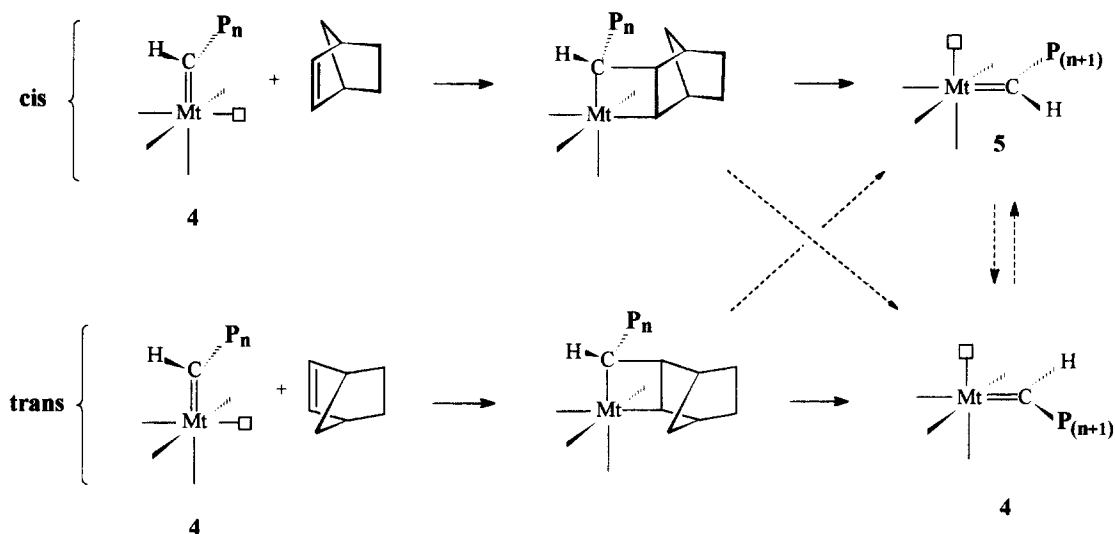
well defined, single-component, W, Mo and Ru-based initiator systems; remarkable degrees of control of polymer microstructure and molecular weight have been achieved^{16–19}. However, the precise factors that control polymer stereochemistry, particularly tacticity, are still the subject of debate and therefore the methods which one can use for its determination are important to the whole metathesis polymerization field.

The great majority of metathesis polymers are formed either from bicyclo[2.2.1]hept-2-ene (norbornene), **2**, or from other monomers based on this ring system, and in fact the detailed study of tacticity in ROMP is based exclusively on these materials. On ring opening, these monomers give the cyclopentylenevinylene repeating unit, and tacticity then arises as a result of the relative orientation in which neighbouring cyclopentylene rings are enchainned. Thus, *meso* (*m*) or *racemic* (*r*) junctions may be formed and the tacticity of a particular dyad unit is defined by reference to the relative configuration of neighbouring allylic carbon atoms in adjacent cyclopentylene rings, in a manner analogous to that used to describe the various stereochemical permutations in poly(propylene) (Scheme 1).

Although n.m.r. spectroscopy, particularly ^{13}C n.m.r., has been used extensively in the analysis of ROMP polymers, most literature reports are confined to information relating to variations in the *cis/trans* double bond ratio, the microstructure feature which is usually responsible for the main spectral line splitting. Fine structure due to tacticity, when present, may be submerged in that due to *cis* and *trans* double bonds, making tacticity in most ROMP polymers less easily determined than in the cognate field of Ziegler–Natta polymerization. Also, neighbouring chiral centres are more remote than in the latter case so, whilst one may routinely observe pentad structures in polymers formed from α -olefins², dyad and triad structures are the more usual limits in the spectra of ROMP polymers^{5,6}. A further complication is that there is no direct relationship between double bond stereochemistry and dyad tacticity, so *cis* or



Scheme 1 Microstructural variations in polymers formed by ring-opening metathesis polymerization (ROMP) and Ziegler-Natta polymerization



Scheme 2 A mechanism for the formation of *cis* syndiotactic and *trans* isotactic ROMP polymers

trans lines in the spectra may have varying *m* and *r* components. Nevertheless, given the high profile of the Ziegler-Natta studies and the contemporaneous development of the ROMP reaction, it is somewhat surprising that the question of tacticity in the latter was not seriously addressed until the studies of Ivin and Rooney in the late 1970s, which were the first systematic investigations of tacticity in the field²⁰⁻²².

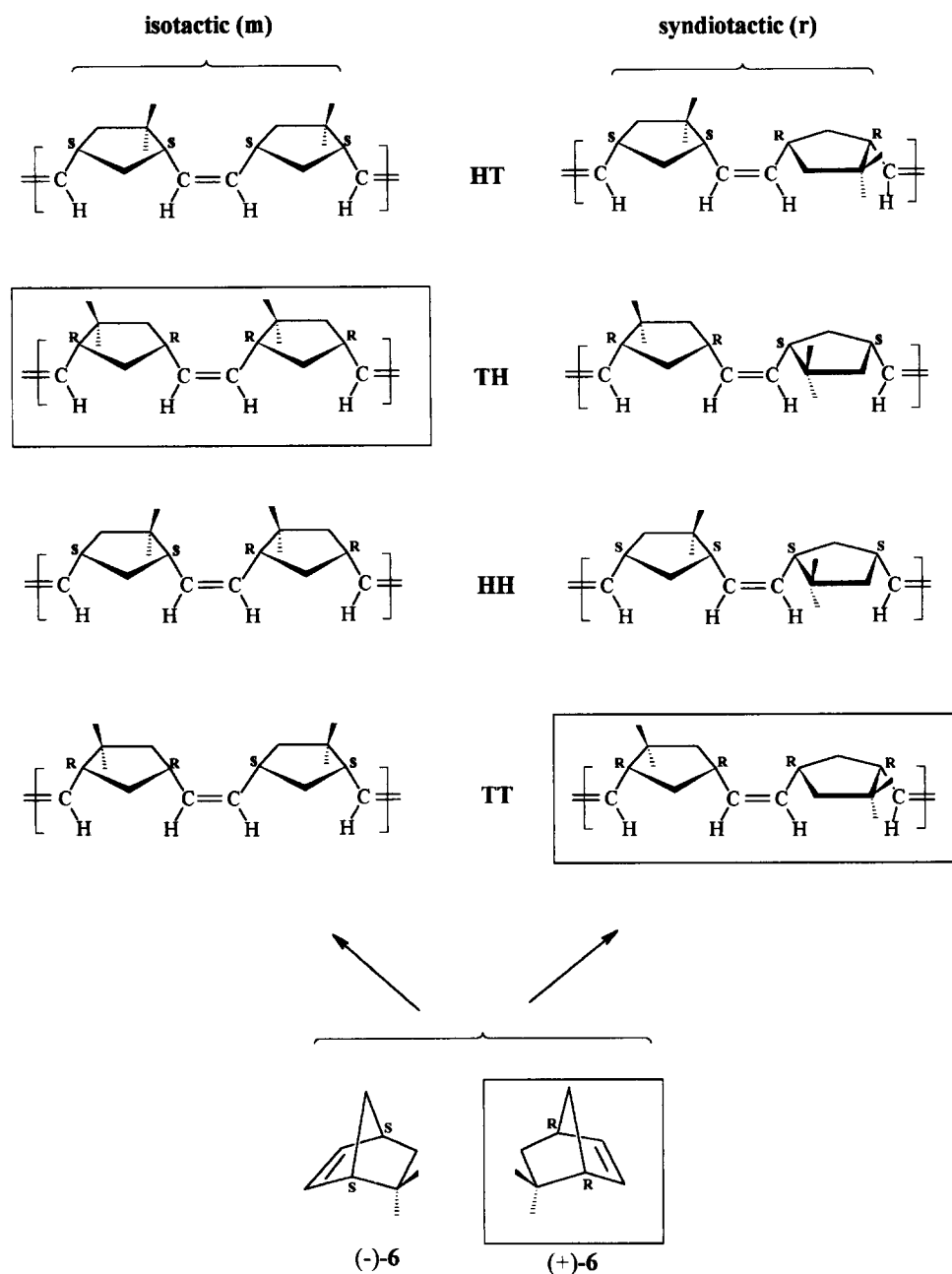
This article attempts to provide an overview of a methodology, based principally on ¹³C n.m.r. spectroscopy, which has been developed and applied to the determination of the tacticity of numerous polymers produced by the ROMP reaction. Mechanistic aspects of the propagation reaction, which have either provided the initial stimulus for

the microstructural studies or have evolved from them, are also considered.

The methods are described in roughly chronological order. Thus unambiguous determination of tacticity, using polymers formed from single enantiomers, is examined first and this is followed by sections dealing with polymers formed from symmetrical monomers and hydrogenated derivatives where the estimation of polymer tacticity is indirect.

DETERMINATION OF TACTICITY USING OPTICALLY ACTIVE MONOMERS

It is possible in many instances to make an assessment of a



Scheme 3 Relationship between orientational bias and tacticity in the formation of *cis* polymers from (\pm)-6 and (+)-6

metathesis polymer's tacticity from an initial inspection of its ^{13}C n.m.r. spectrum. This is based on the degree and pattern of splitting of the main resonances and is most valuable if one has available tactic and atactic forms to make a comparison, especially if all the double bonds in these polymers are either *cis* or *trans*, as this effectively removes a layer of fine structure from the spectra. It is, however, important to be aware of the fact that the absence of fine structure, even in high *cis* and high *trans* cases, does not necessarily imply stereoregularity, and also that it is not possible to make absolute assignments in terms of syndiotactic, *r*, or isotactic, *m*, structures directly from the ^{13}C n.m.r. spectra.

Several methods, however, have been developed which allow the absolute assignment of tacticity, each of these involve the polymerization of optically active monomer and the same underlying principle, that of the symmetry of the different dyad units, governs each of these methods. Thus, in polymers formed from single enantiomers, syndiotactic

dyad structures possess a C_2 axis in the plane, or perpendicular to the plane, of a given double bond; this is absent in isotactic structures irrespective of the stereochemistry of the double bond. The polymer tacticity may therefore be determined through the medium of the n.m.r. spectra of equivalent or inequivalent olefinic carbon atoms and protons in these units.

The following sections describe these methods from a historical and mechanistic perspective.

Polymerization of (+)-5,5-dimethylnorbornene

The first of these methods developed as a result of detailed considerations of the implications for tacticity of a polymerization mechanism that permitted the formation of both *cis* and *trans* double bonds at an essentially enantiomeric catalyst site²⁰. A basic mechanism, Scheme 2, involving propagation by octahedral complexes, such as **4**, with vacant ligand sites for monomer coordination, analogous to those believed to be responsible for

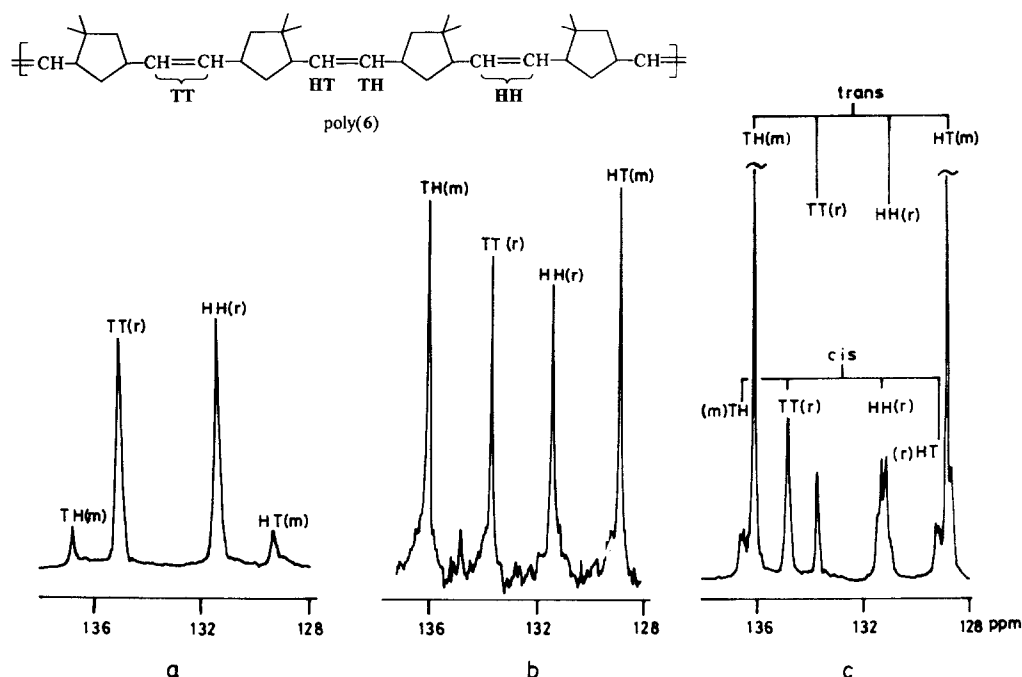


Figure 1 Olefinic region of the ^{13}C n.m.r. spectrum of poly((+)-6): (a) high-*cis* syndiotactic polymer; ReCl_5 catalyst; (b) high-*trans* atactic polymer, RuCl_3 catalyst; (c) 75% *trans* isotactic/25% *cis* syndiotactic polymer, (mesitylene) $\text{W}(\text{CO})_3/\text{EtAlCl}_2$ catalyst. (a) and (b) reprinted from Ho, H.T., Ivin, K.J. and Rooney, J.J., *Makromol. Chem.*, 1982, **183**, 1629, by permission of Hüthig & Wepf Publishers, Zug, Switzerland; (c) reproduced from Devine, G.I., Ivin, K.J., Mohamed, M.A. and Rooney, J.J., *J. Chem. Soc. Chem. Commun.*, 1982, 1229, by permission of the Royal Society of Chemistry.

Ziegler–Natta polymerization, was proposed^{20,23}. This, along with the stipulation that reaction occurred at the *exo* face of the norbornene molecule, later shown to be the case by polymerization studies of *syn* and *anti* 7-methylnorbornene, *vide infra*, were the primary mechanistic assumptions.

The propagating metallocarbene, **4**, is chiral with respect to the metal centre and so formation of a *cis* double bond, via a metallacyclobutane intermediate or transition state, leads to a site of opposite chirality, i.e. **5**, whereas the chirality of the site is retained after *trans* double bond formation (Scheme 2).

Alternative, contemporary, theories²⁴, which interpreted *cis/trans* ratios solely in terms of different conformations of intermediate metallacyclobutanes formed from a *single* metallocarbene species, were the result of studies on acyclic olefins and could not therefore address the problem of polymer tacticity, although the different modes of opening the metallacycle are now considered to be important to both cyclic and acyclic metathesis²⁵. More recently, certain well defined metallocarbene complexes which initiate ROMP have been shown to exist in *syn* and *anti* forms, and the stereochemistry of the propagation reaction is believed to be controlled by their kinetic accessibility^{18,26,27}. Different relative rates of propagation and *syn/anti* isomerism could potentially yield polymers with a blocky distribution of *cis* and *trans* double bonds, a feature which has been extensively studied with the classical catalysts⁶.

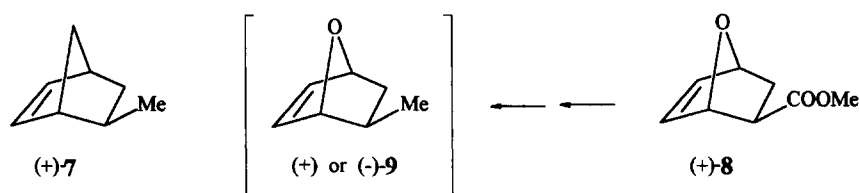
A direct consequence of the basic Ivin–Rooney mechanism is that if there is no loss of chiral identity through processes such as ligand exchange, simultaneous formation of **4** and **5** on metallacycle rupture, or rotations around the metal carbon bond, *cis* double bond formation should be associated with syndiotacticity and *trans* with isotacticity²⁰. Initially studies were carried out with norbornene, **2**, but, although a number of high *cis* and high *trans* samples of poly(**2**) were available, fine structure, which could be attributed to tacticity, was not observed in the spectra of the polymers, so in order to test the theory some alternative

means of detection was necessary. In fact the observation of tacticity in the prototypal poly(**2**), or more correctly its hydrogenated derivative, is a recent development dependent on instrumentation not available at the time, and will be discussed later.

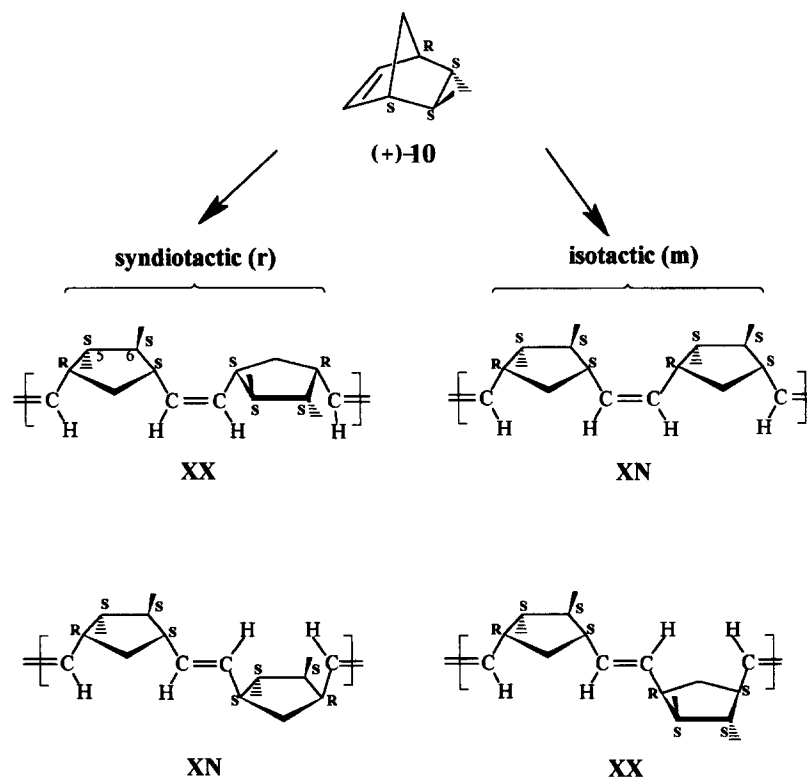
Careful consideration of the proposed mechanism revealed that if single enantiomers of unsymmetrically substituted norbornene derivatives were polymerized the type of tacticity would be revealed as an orientational bias of the substituents in the various ring dyad units embracing the double bond, so the tacticity of the polymer could be determined from its ^{13}C n.m.r. spectrum provided that the polymerization of the racemic mixture did not result in any significant orientational bias^{21,22}. The validity of this method lies in the correct assignment of the spectral lines, and so an exhaustive analysis of the spectra was performed²².

The methodology is illustrated in Scheme 3 for the formation of polymers from (+)-5,5-dimethylnorbornene, (+)-**6** (N.B., the absolute stereochemistry of the monomer is not known but an arbitrary assignment of (+)-1R, 4R will suffice for the purposes of the argument).

Scheme 3 depicts the eight possible dyad units which can embrace *cis* double bonds in an atactic polymer formed from both enantiomers of 5,5-dimethylnorbornene; head-to-tail (HT) and tail-to-head (TH) structures, although shown in the Scheme as separate units, are indistinguishable in the n.m.r. spectrum, and are distinguished only from the point of view of the *direction* of propagation. Although the scheme shows only *cis* double bonds the case for *trans* double bonds is identical, making a grid of sixteen possible dyad structures, and it can be seen that when both enantiomers are used the substituent orientation may be either HT(TH), HH or TT irrespective of the tacticity of a given junction. However, if we are restricted to the polymerization of only one enantiomer, e.g. the RR isomer, then an all-*cis* isotactic polymer must necessarily consist of only HT (TH) units and an all-*cis* syndiotactic



Scheme 4 Optically active **7** and **9** may be used to determine the influence of proximal oxygen atoms on the stereochemistry of the propagation reaction



Scheme 5 Dyad units which may be formed in the polymerization of single enantiomers of **10**

polymer of only TT and HH units (N.B., the HH unit is formed on addition of another RR enantiomer to the TT unit). This also applies when considering an all-*trans* polymer. It is important to stress here that in this analysis, for a given monomer/catalyst combination, the polymer *tacticity* is not in any sense dependent on the optical purity of the monomer; polymerization of single enantiomers merely allows tacticity to be revealed as an orientational bias of substituents.

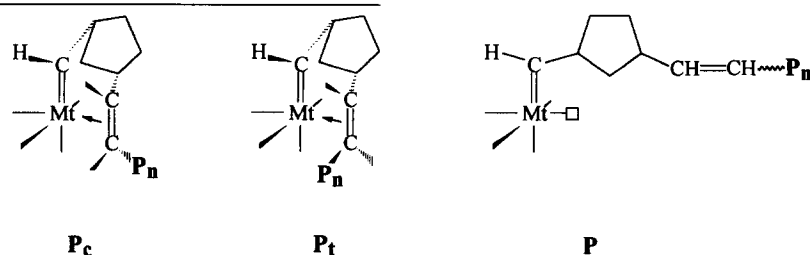
The proportion of each of these units is most readily detected in the olefinic region of the ^{13}C n.m.r. spectra of the polymers, and the interpretation of the spectra is greatly facilitated by the large chemical shift difference of the olefinic carbon atoms which, with respect to poly(**2**), have either two γ substituents (the head carbon) or are unsubstituted in this respect (the tail carbon)²².

The ^{13}C n.m.r. spectrum shown in Figure 1a is that of a high *cis* polymer produced from (+)-**6** with the ReCl_5 catalyst and shows predominantly HH and TT signals, indicating that the polymer is syndiotactic; the small HT and

TH signals are attributable to the presence of 7% of the (–) enantiomer. In contrast, the high *trans* polymer, produced with the RuCl_3 catalyst, Figure 1b, has HT(TH), HH and TT units in equal proportion and is therefore atactic.

The behaviour of a whole range of classical catalyst systems was investigated by this method and a number of different microstructural types were recognised; it was found generally that whereas *cis* junctions were frequently associated with syndiotacticity, *trans* junctions tended to be atactic. This, combined with the fact that the distributions of *cis* and *trans* double bonds in medium to high *cis*-content polymers were blocky, led to a substantial modification of the original mechanism shown in Scheme 2; subsequently, quite elaborate schemes were suggested in order to rationalize these observations.

In essence, it was argued that the metallocarbene, **4**, can exist in the kinetically distinct forms P_c , P_t and P , distinguished by the nature and location, with respect to the metal, of the last formed double bond.



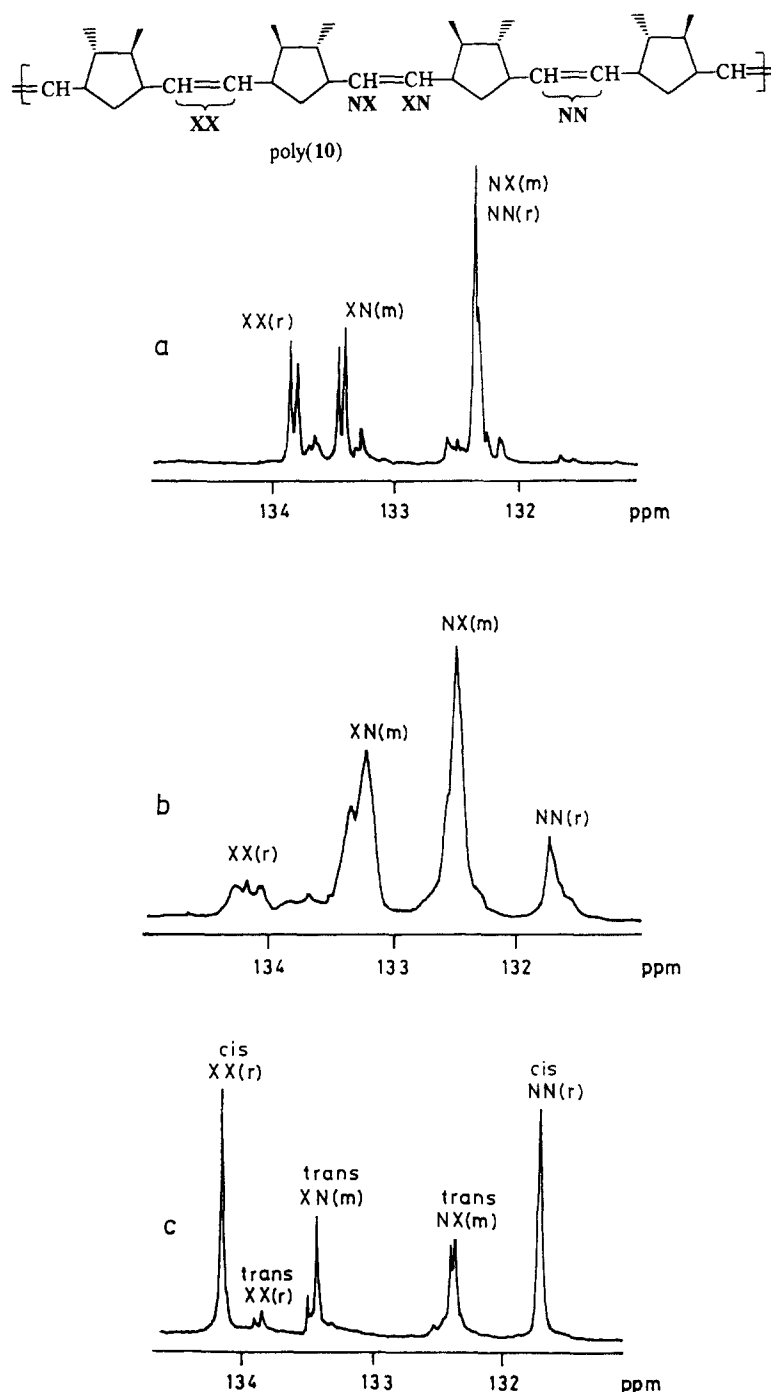


Figure 2 Olefinic region of the ^{13}C n.m.r. spectrum of poly((+)-10): (a) 5% *cis* atactic polymer, catalyst **11**; (b) 85% *cis* isotactic polymer, catalyst **12**; (c) 90% *cis* syndiotactic polymer, $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$ catalyst. (a) and (b) reproduced with permission from Sunaga, T., Ivin, K.J., Hofmeister, G.E., Oskam, J.H. and Schrock, R.R., *Macromolecules*, **27**, 4043. © 1994 American Chemical Society

The species \mathbf{P}_t , which has the last formed (*trans*) double bond in the coordination sphere of the metal, would, due to steric demands, be inaccessible to monomer and must relax to a form \mathbf{P} , symmetrical with respect to the carbene carbon and the metal centre, in which the last double bond has left the coordination sphere. It was postulated that \mathbf{P} reacts with monomer to form mainly *trans* double bonds and, by virtue of its symmetry, leads to equal numbers of *m* and *r* junctions. In this scheme *cis* syndiotactic polymer is formed via the species \mathbf{P}_c which can propagate the reaction with the last formed *cis* double bond still in the coordination sphere of the metal. Addition of the next monomer unit then takes place in such a way as to form another *cis* double bond, epimerization at the metal centre being retarded by the coordinated *cis* double bond which may provide an

additional stereochemical lock. The theories outlined here provided a rationale for the formation of blocky polymer, i.e. *cis* after *cis* and *trans* after *trans*, whilst accommodating different polymer tacticities²⁸.

Within this context, an interesting development was the formation of a high *trans* isotactic polymer using a particularly active catalyst system based on (mesitylene)- $\text{W}(\text{CO})_3$ with an EtAlCl_2 cocatalyst²⁹. This produced isotactic *trans* junctions and syndiotactic *cis* junctions, Figure 1c, behaviour which has since been observed in the polymerization of several other monomers using this catalyst, *vide infra*. It was reasoned that, at least in this case, the chiral \mathbf{P}_t or some form derived from it, in which the chiral identity is retained, was a chain carrier; relaxation to symmetrical forms such as \mathbf{P} being slow compared to propagation.

It can be seen from *Figure 1* that the chemical shift difference between the head and tail carbon signals in these spectra is such that they are resolved at the baseline and, fortuitously, the sets of lines from *cis* and *trans* double bonds are substantially free from overlap. This fact was of primary importance to the method because most catalyst systems in fact produced polymers which contained comparable proportions of *cis* and *trans* double bonds and therefore the tacticity associated with each kind of junction could be estimated, as is illustrated by reference to *Figure 1c*.

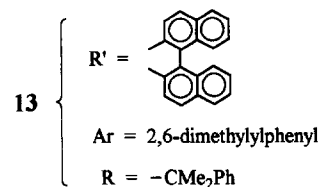
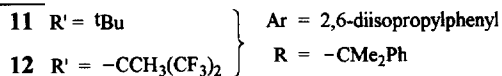
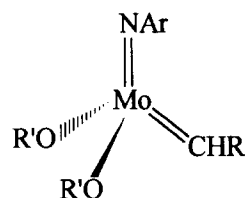
Initial studies in this area were conducted using (+)-*exo*-5-methylnorbornene **7**²¹ and, although similar results were obtained, the monomer was less accessible synthetically and the spectra of the polymers were less well resolved; it was therefore abandoned in favour of **6**. However, a recent synthetic development³⁰ has made available nearly optically pure **8** which could conceivably be converted to **9**, the oxabridged analogue of **7** (*Scheme 4*). The tacticity of poly(**7**) and poly(**9**) prepared using various catalysts could then be directly compared and the effect of an oxygen bridge in the monomer on polymer tacticity studied. It is already recognised that a proximate oxygen atom can have profound effects on the ROMP propagation process^{31–33}.

In summary, (+)- and (–)-**6**, despite a somewhat tedious synthesis, are excellent monomers for tacticity determination in ROMP. Their high reactivity means that they can be used with a wide variety of catalyst systems and the high quality of the spectra of the polymers facilitates the determination of the tacticity not only in high *cis* and high *trans* cases but in polymers of intermediate *cis* content. Also, it is clear that this method may be used for other

methyl substituents on adjacent cyclopentylene rings may have either the same or opposing orientations, leading respectively to *exo,exo* (XX), *endo,endo* (NN) or *exo,endo* (XN) dyad units (*Scheme 5*).

An exercise similar to that portrayed in *Scheme 3* reveals that although polymers formed from (+)-**10** give XN *cis* isotactic dyads and XX/NN *cis* syndiotactic dyad units, analogous to the HT and HH(TT) units in polymers of **6**, the reverse is the case for *trans* isotactic dyads, which are XX/NN biased, and *trans* syndiotactic dyads, which are XN biased. This apparent contradiction is a result of the nature of the substitution at C5 and C6. In poly(**10**), C5 and C6 each bear one methyl substituent so the symmetry or otherwise of the dyad and hence the tacticity is determined solely by the relative configuration at C1, C5 and C4, C6. In poly(**6**) it is the relative position of the *gem*-dimethyl substituents which allows one to determine the tacticity. In both cases it is the symmetry of the dyad unit which is important.

Initial studies of these polymers were carried out using classical catalyst systems with racemic monomer and it was observed that only high *trans* polymers were formed. This contrasts with the behaviour of the corresponding *endo,endo* and *exo,exo* monomers which gave polymers with a complete range of *cis* double bond contents³⁵. A more recent study³⁴ using the Schrock metallocarbene **11** and **12** produced polymers with an extended range of *cis* double bond contents as a function of the nature of the alkoxy ligand; with **12**, which has the more electronegative partially fluorinated 'butoxy ligand, a higher *cis* content polymer was obtained, although it was still not possible to exceed 85% *cis*.



monomers which are not norbornene based but which contain asymmetric substituents and give polymers with main chain chirality, for example appropriately substituted cyclobutenes, cyclooctenes and cyclopentenenes. The main requirements are that substituent orientation is detectable in the ¹³C n.m.r. spectra of the polymers and that they are available in a fairly high degree of optical purity.

Polymerization of (+)-*endo,exo*-5,6-dimethylnorbornene

A subtle variation on the use of substituent orientation as a means of determining tacticity may be seen in polymers formed from (+)-*endo,exo*-5,6-dimethylnorbornene, (+)-**10**³⁴ (*Scheme 5*). Although the spectra of the polymers (*Figure 2*) are sometimes less well resolved than is usually the case of polymers formed from **6**, the method of monomer preparation is simpler, involving an asymmetric Diels–Alder reaction which yields eventually a 96% ee product whereas the preparation of **6** involves the notoriously protracted optical resolution by crystallization of diastereomers which gives a much smaller yield and lower optical purity.

In polymers formed from this monomer, neighbouring

Using the optically active form of the monomer, it was demonstrated that high *trans* polymers prepared using **11** showed no XN or XX/NN bias and were therefore atactic (*Figure 2a*), as is the case with most classical catalysts. However, whilst high *cis* polymers, formed using initiator **13** (*Figure 2b*), were found to be strongly XN biased and therefore isotactic³⁶, an OsCl₃ catalyst, modified with PhC≡CH, produced a 61% *cis* polymer with syndiotactic junctions, which is demonstrated by the XX, NN bias in the spectrum of the polymer (*Figure 2c*)³⁷; the *trans* junctions here appear to be largely isotactic and the polymer has a very blocky distribution of *cis* and *trans* double bonds.

One of the features which is beginning to emerge from tacticity studies in general is the apparently divergent behaviour of classical and preformed, metallocarbene-type, initiators. The latter tend to give isotactic *cis* and syndiotactic or atactic *trans* polymers^{27,37} whereas the classical systems have been shown generally to give the reverse^{38,39}. The polymerization studies with **10** described above are important in that they show clearly that this is not merely a result of the different methods used to determine tacticity but that it may have a more fundamental and

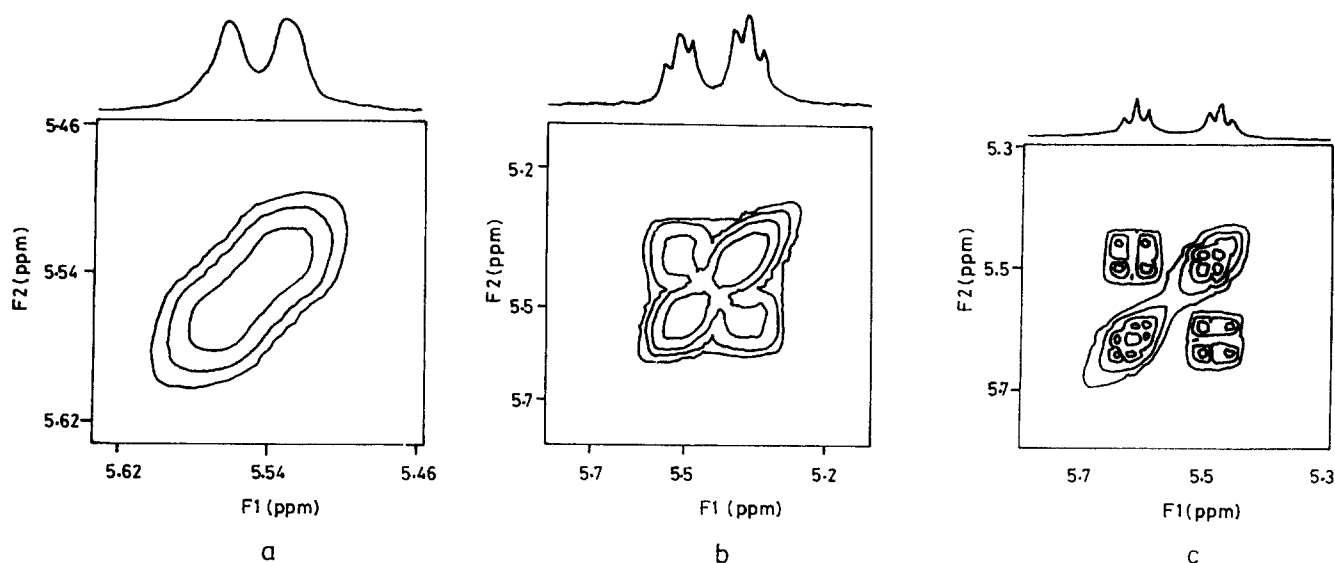


Figure 3 Olefinic region of the homonuclear (proton/proton) correlation (COSY) spectra of (a) high-*trans* syndiotactic poly(**14**), catalyst **11**; (b) high-*cis* isotactic poly(**14**) catalyst **12**; (c) high-*cis* isotactic poly(**10**), catalyst **13**. Reproduced with permission from O'Dell, R., McConville, D.H., Hofmeister, G.E. and Schrock, R.R., *J. Am. Chem. Soc.*, **116**, 3414. ©1994 American Chemical Society

interesting explanation. For example, as is the case in Ziegler–Natta polymerization, the physical state of the catalyst may be important⁴⁰. Classical systems which produce tactic polymer, i.e. ReCl_5 ²², $\text{W}(\text{mesitylene})(\text{CO})_3/\text{EtAlCl}_2$ ²⁹ and $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$ ³⁷, as prepared, are suspensions and the catalysis may well be heterogeneous, whereas metallocarbene catalysts are more often present as homogeneous solutions, so the physical state may play an important role in determining a catalyst's stereoselectivity. Given the options for tacticity determination described herein, this aspect of metathesis polymerization may now be fully investigated.

Polymerization of optically pure 2,3-dicarboxyalkoxy-norbornadienes

Each of the methods described above makes use of monomers which are chiral due to an unsymmetrical substitution pattern on the norbornene ring system, a necessary structural requirement if one is to observe orientational bias in the respective polymers. The monomer synthesis, however, involves either optical resolution or asymmetric synthesis which may be quite time consuming and, although the ability of a given catalyst to produce *cis* or *trans*, syndio, iso or atactic polymer may be assessed unambiguously, the methods are indirect.

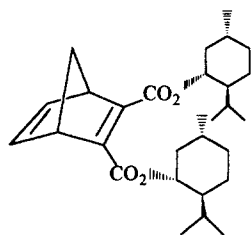
The most recent development in the field comes from the laboratories of R. R. Schrock, where an elegant direct ¹H n.m.r. method has been developed³⁶. Here again, use is made of optically active monomers, in this case norbornadiene derivatives containing chiral alkoxy substituents, **14** and **15**, which are derived from readily available optically active alcohols, so that the optically active monomer is obtained directly in high enantiomeric excess. In essence these monomers are, from the

point of view of the current methodology, equivalent to (+)-**10**, the major difference being that the chiral centres within individual repeating units are now more remote.

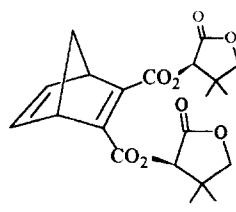
The olefinic region of the ¹H n.m.r. spectrum of a high *cis* polymer (Figure 3b) formed from this monomer shows two resonances which arise from inequivalent olefinic protons; the spectra of *trans* polymers are similar (Figure 3a), though less well resolved. Consideration of the symmetry of the four possible stereochemical environments in which these inequivalent protons may exist (Scheme 6) reveals that they reside on adjacent double bonds in syndiotactic dyads, and are therefore not coupled, but on the same double bond in isotactic dyads, where they are coupled. The argument applies to both *cis* and *trans* double bonds.

The presence, or absence, of coupling was detected by the presence of cross-peaks in routine COSY experiments, Figure 3a and b, carried out on polymers prepared using initiators **11** and **12**, and it was determined that whereas the high *trans* polymer prepared using **11** was, atypically, syndiotactic (Figure 3a), **12** produced an isotactic high *cis* polymer (Figure 3b).

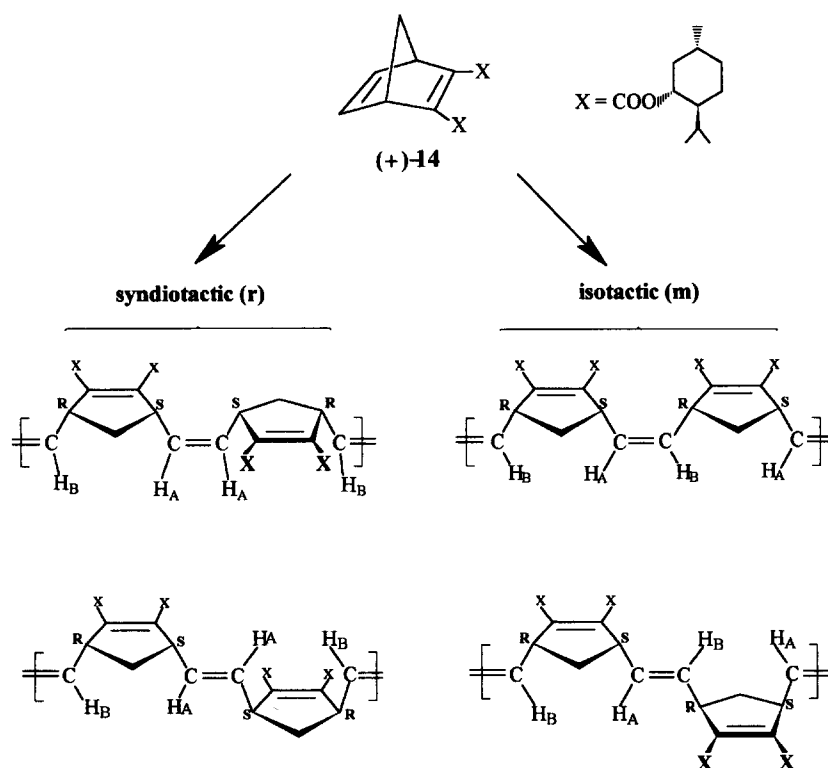
The method will therefore allow one to distinguish unambiguously between catalysts which produce highly syndiotactic and highly isotactic polymers which are either high *cis* or high *trans*, but it would be of less benefit in determining the degree of tacticity in intermediate *cis* content polymers where olefinic signals might well overlap. Also, one would have difficulty in making a distinction between, for example, a highly isotactic and an atactic polymer, solely on the basis of their COSY spectra, because both polymers would show cross-peaks as both contain isotactic dyads. Whilst a similar experiment could clearly be



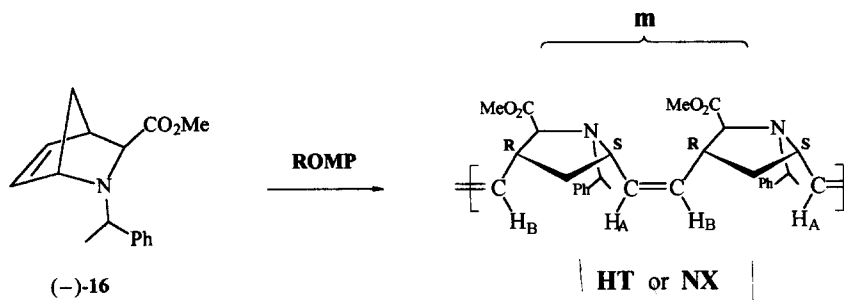
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15



Scheme 6 Equivalent and non-equivalent vicinal olefinic protons in dyad units of different tacticity which may be formed in the polymerization of (+)-14



Scheme 7 Formation of a high *cis* content, isotactic, poly(amino acid) analogue by ROMP

used for tactic polymers formed from single enantiomers of 5,5-dimethylnorbornene (Scheme 3), it would, unlike the ^{13}C n.m.r. method described earlier, be again restricted to high *cis* and high *trans* cases.

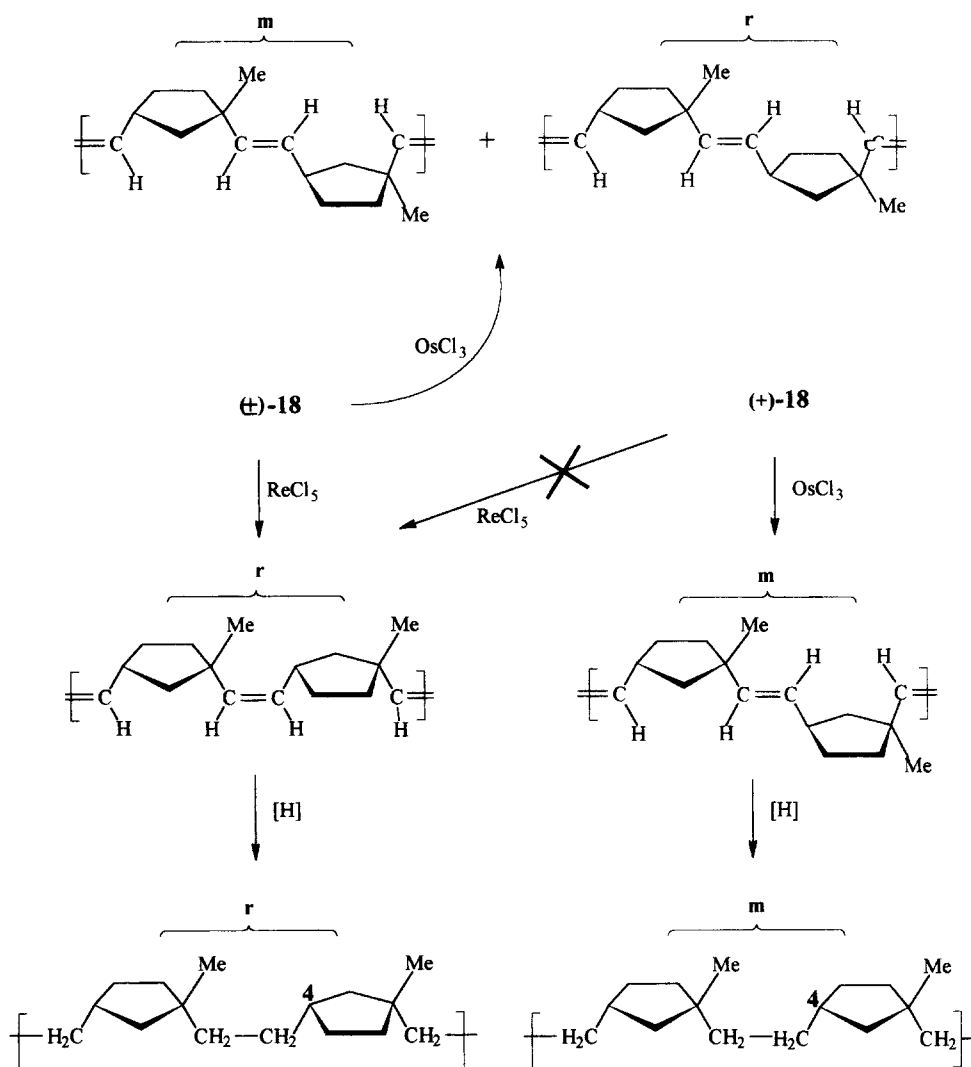
Well resolved ^{13}C n.m.r. spectra³⁶ are reported for tactic polymers formed from 14 and 15, and, because the COSY experiments have permitted definition of the tacticity, the position of the *m* and *r* ^{13}C n.m.r. resonances for both *cis* and *trans*-centred dyads is known with certainty. Using the general methodology described herein this provides the basis for the analysis of the ^{13}C n.m.r. spectra of microstructurally more complex polymers.

The method was also applied to polymers formed from (+)-10 and so a particularly valuable aspect of this study was that it permitted correlation of two different methods of tacticity determination, both using a given polymer sample³⁶. Thus the COSY spectrum of high *cis* poly(10) formed using 13 as initiator (Figure 3c) showed, by virtue of well resolved cross-peaks, that the olefinic protons were coupled, meaning that the polymer was isotactic, entirely consistent with the strong XN bias in the same polymer as seen in its ^{13}C n.m.r. spectrum. Unfortunately, a high *cis* syndiotactic polymer, which should not show a cross-peak, was then unavailable for direct comparison.

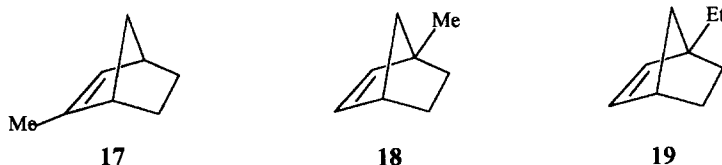
The method has been applied recently to the determination of tacticity in a novel poly amino acid analogue formed from the azanorbornene derivative (-)-16⁴¹ (Scheme 7). Using a Schrock-type Mo initiator related to 12 (R = ^tBu), a high *cis* polymer was formed which was again shown to be isotactic from the existence of cross-peaks in the olefinic region of the COSY spectrum. Although the authors, with justification, view the dyad units in this polymer as HT, it is worth noting that the polymer is exactly analogous to poly(10) because of the relative configuration of the substituents at the 2 and 3 positions, so it may also be considered as an XN biased polymer.

Polymerization of 1-methylnorbornene

The methodology described above for poly(6) and poly(10) relies on there being little or no inherent regioselectivity during the propagation reaction of the racemic monomer; in fact, substituents in the 5 and 6 positions in norbornene are sufficiently remote from the reaction site so that only a minimal head-to-tail (HT) bias is evident³⁸. In contrast, placement of an alkyl substituent on the double bond in norbornene, as in 17, results in complete regioselectivity⁴² whereas intermediate, and catalyst dependent, regioselectivity is observed when the substituent is at



Scheme 8 Formation of atactic, isotactic and syndiotactic poly(1-methylnorbornene), poly(**18**); demonstration of the syndiotacticity of the polymer formed using the ReCl_5 catalyst



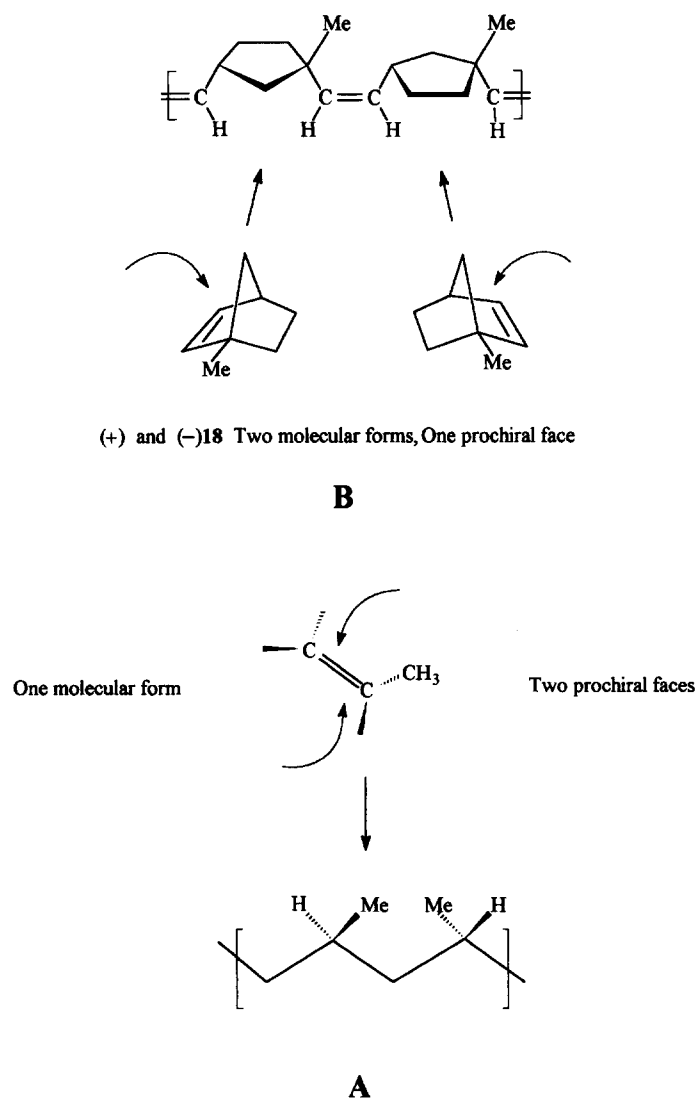
the bridgehead position as in 1-methylnorbornene, **18**^{43,44}. Such monomers are therefore not suited for tacticity determination, but the special case of the polymerization of **18** is not entirely out of context because of the unique nature of certain polymers that were obtained from it and because it was necessary to use optically active monomer in the analysis⁴⁵.

Polymerization of **18** with the ReCl_5 catalyst produced the expected high *cis* polymer whereas the RuCl_3 , as well as OsCl_3 , catalyst produced high *trans* polymers. ReCl_5 and OsCl_3 both behaved in a completely regioselective manner giving essentially all HT, *isoregic*⁴⁶ polymers, whereas RuCl_3 was totally non-selective in this respect and a polymer with a random orientation of substituents was obtained⁴⁴.

With these polymers a different approach to tacticity determination was necessary because their spectra, with the instruments available at the time of the initial studies, did not show any fine structure attributable to tacticity, although

it is significant that polymers formed from the more sterically constrained 1-ethyl derivative, **19**, did exhibit the effect⁴⁷. The method of polymerization of enantiomers, *per se*, was also inappropriate because of inherent HT bias. Hydrogenation, *vide infra*, of the double bonds in the all-HT polymers, however, yields materials in which tacticity is the only possible microstructural variable. It was found that in the spectrum of the hydrogenated polymer from the OsCl_3 catalyst the C4 resonance was a doublet whereas the same resonance in the hydrogenated polymer from the ReCl_5 catalyst appeared as a single sharp line, indicating that whilst the former polymer was atactic the latter polymer was tactic⁴⁵. According to the propagation mechanism outlined in *Scheme 2* the polymer should be syndiotactic, and again this was shown to be the case by resorting to the polymerization of the resolved monomer (*Scheme 8*).

The *trans*, all-HT, polymer prepared from (+)-**18** using OsCl_3 is necessarily isotactic. Accordingly, the C4 resonance in the ¹³C n.m.r. spectrum of its hydrogenated



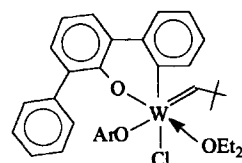
Scheme 9 Formation of syndiotactic poly(propylene) and syndiotactic poly(1-methylnorbornene)

derivative appeared as a single sharp line, the *m* signal, and was coincident with the upfield component of C4 in the spectrum of the polymer formed from (\pm)-**18** using OsCl_3 , meaning that the downfield component must be an *r* line. This line was coincident with the single line in the spectrum of the ReCl_5 -formed polymer after hydrogenation, thus proving its syndiotacticity. The analysis meant that in the polymerization of (\pm)-**18** the Re site was behaving with complete stereoselectivity, choosing a different enantiomer in each subsequent propagation cycle, and it was highly significant that attempts to polymerize (+)-**18** using ReCl_5 were unsuccessful. The reaction was the first example of alternating copolymerization of enantiomers.

The parallels drawn between Ziegler–Natta and ROMP polymerizations earlier are reinforced by this result because the metathesis polymerization of **18** is analogous to the formation of syndiotactic polypropylene (Scheme 9A). In the latter reaction the catalyst chooses a different prochiral face of the monomer, which exists in only one molecular form, in successive propagation steps whereas, in the former (Scheme 9B), the catalyst, which is constrained to react at the *exo* face, chooses a different molecular form, (+)-**18** or (–)-**18**, in successive propagation steps.

The initial studies were carried out on a 62.6 MHz instrument but more recently poly(**18**) was examined at 125 MHz. The spectrum of the polymer produced using

ReCl_5 showed only eight sharp lines (Figure 4a), characteristic of its highly syndiotactic nature, in contrast to all-*cis*, all-HT poly(**18**) prepared using a well defined cyclometallated tungsten catalyst, **20**^{5,48}. This polymer gave the spectrum shown in Figure 4b, and exhibited extensive fine structure for all but one resonance, consistent with its being only partially syndiotactic. The polymer is somewhat stereoblocky and this can be shown by a simple calculation based on the intensity pattern of the C1 and C7 signals. The overall *r*:*m* ratio can be determined from the C1 doublet and, based on this, a random *m*/*r* distribution should give an intensity ratio at C7 of 4:2:2:1 whereas the observed ratio is approximately 3:1:1:1, consistent with the occurrence of blocks of *r* and blocks of *m* in the polymer. Another interesting feature of this spectrum is the eight-component C2 resonance, which must arise from a sensitivity to ring tetrad tacticity which has not previously been observed.



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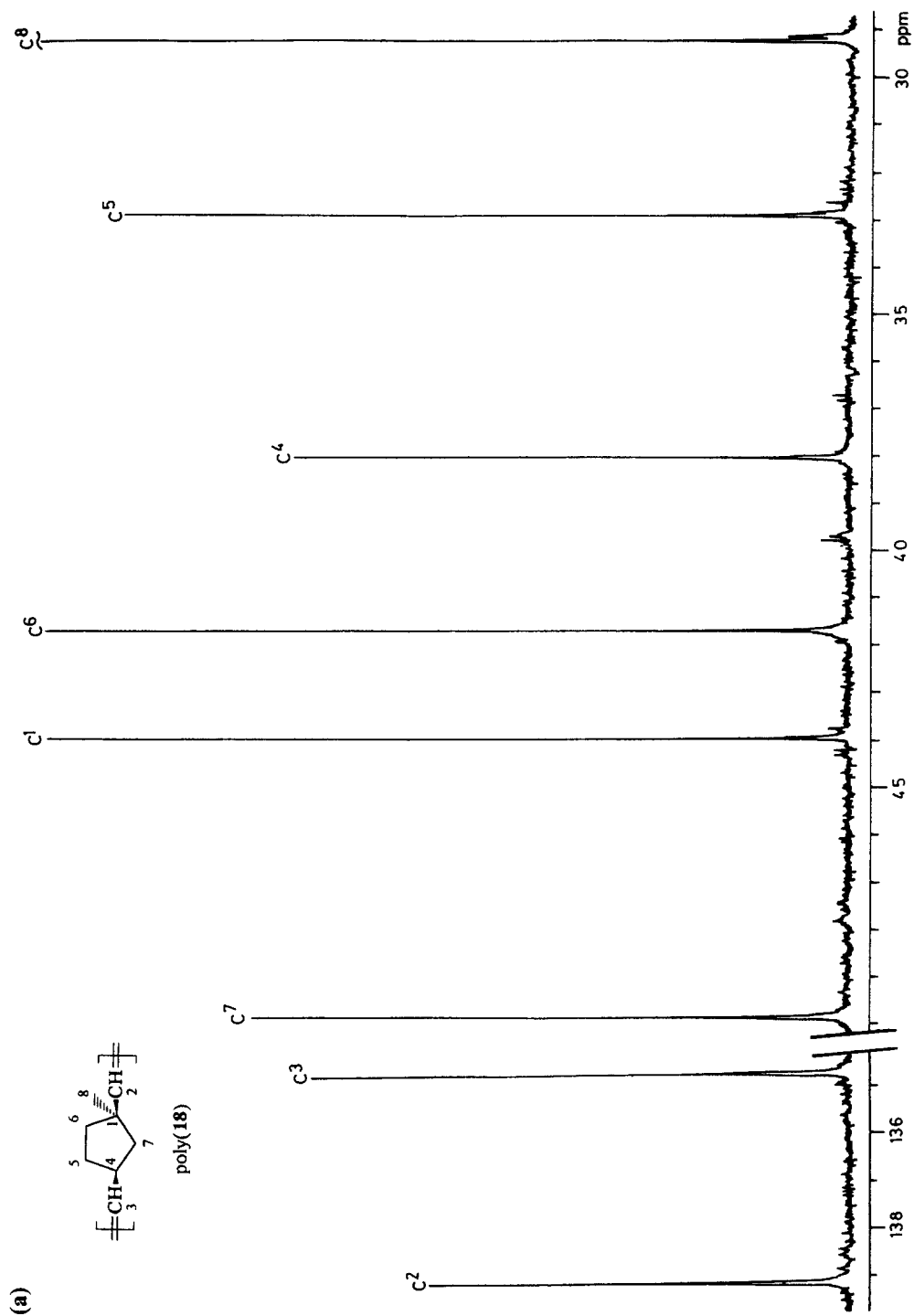


Figure 4 125 MHz ^{13}C n.m.r. spectra of high-*cis* and all head-to-tail poly(18): (a) fully syndiotactic polymer. $ReCl_5$ catalyst; (b) partially syndiotactic polymer, cyclometallated W complex catalyst **20**. Reproduced with permission from Polymer Spectroscopy, A. H. Fawcett (ed.), © John Wiley & Sons Ltd.

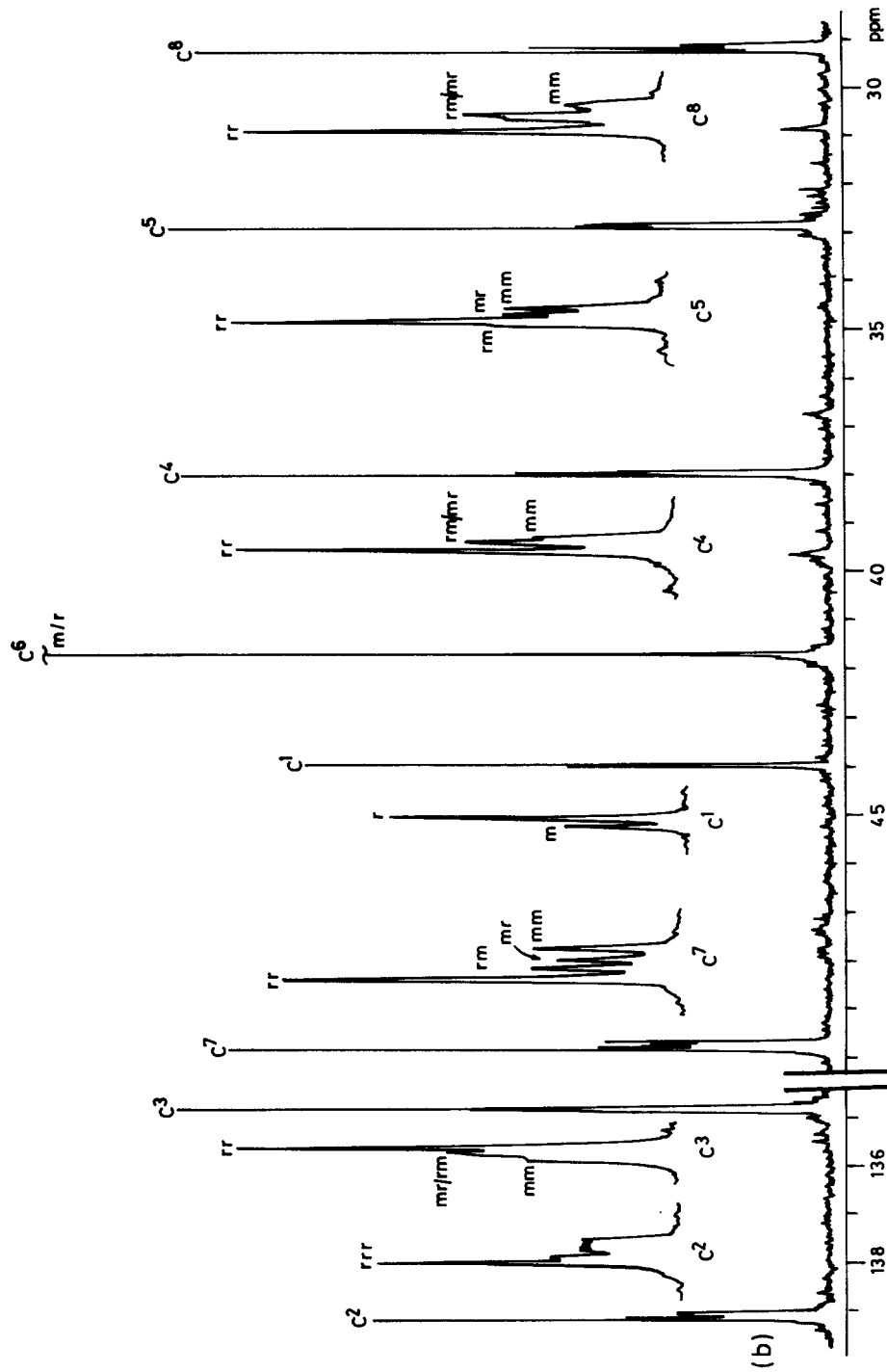


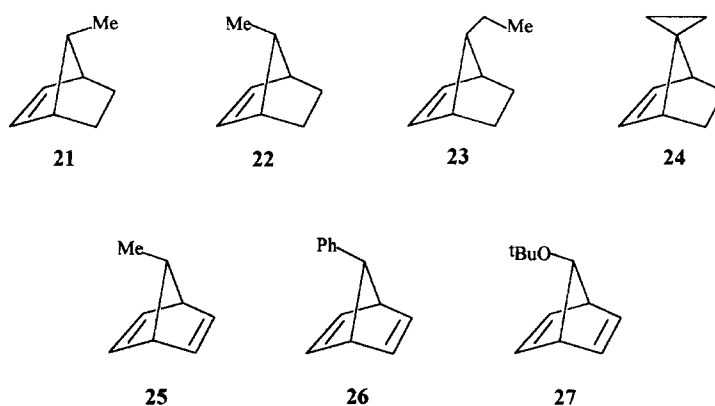
Figure 4 Continued

It is significant that, although polymers formed using ReCl_5 and **20** are both high *cis* and strongly HT biased, only the former is completely tactic, and also that the polymer from the OsCl_3 catalyst, although high-*trans* and strongly HT biased, is atactic. If a mechanism involving a symmetrical metal centre, with control of tacticity being exercised primarily by the last added unit, were operating, i.e. chain end control, it might be expected that tactic polymer would be produced in each case. However, only the polymer from ReCl_5 is fully tactic, which is strong evidence for a mechanism in which control is exercised by a chiral metal centre such as P_c , i.e. enantiomorphic site control. Preformed metallacarbene initiator systems such as **12** which do not contain chiral ligands but give rise to tactic polymer, albeit with different monomers, are believed to do so by the mechanism of chain end control, whereas tactic polymers formed from analogous catalysts bearing chiral ligands are thought to do so by enantiomorphic site control. In contrast, the work with poly(**18**), suggests that control of

derivatives (this may not be valid for more radical variations in the structure of the monomer). The characteristics of each catalyst are then defined from studies with the optically active monomers, as described in the previous section.

Polymers formed from 7-substituted norbornenes and norbornadienes

As is evident from the foregoing account, norbornene, **2**, and indeed many of its derivatives, are ring-opening polymerization monomers *par excellence* due, not only to the high strain energy which provides an enthalpic drive for the reaction, but also to the special reactivity of the double bond, the π -component of which is unsymmetrical with respect to the sp^2 plane, resulting in the greater electron density residing at the *exo* face⁵⁰. The assumption that reaction with an electrophilic metallacarbene takes place at this face was shown to be the case when essentially only the *anti*-isomer, **21**, was found to polymerize from an equimolar mixture of **21** and **22** using a range of metathesis catalysts³⁹.



tacticity resides at the catalyst site. It would therefore be of great interest to make poly(**18**) using **12**.

TACTICITY IN POLYMERS FORMED FROM SYMMETRICAL MONOMERS

In contrast to the ^{13}C n.m.r. spectra of poly(norbornene)⁴⁸ and poly(norbornadiene)⁴⁹, the spectra of many of their derivatives show well resolved fine structure, over and above that arising from *cis/trans* effects, which may be ascribed to different tacticities, this increased spectral resolution arises largely from reduced segmental motion caused by the substituents². However, as pointed out in the previous section, in the spectra of polymers formed from unsymmetrically substituted monomers these benefits are often diminished, except in cases where resolved monomer is used, because one is not always able to differentiate between tacticity effects and longer range effects due to the orientation of substituents. This problem may, however, be overcome by the use of symmetrically substituted derivatives in which the orientational effects are eliminated while the beneficial chain stiffening effects are retained. This section considers different cases where simple alkyl-substituted norbornene and norbornadiene derivatives have been used to great effect in the estimation of tacticity.

It is important to recognise at the outset that these methods do not allow one to determine tacticity in an absolute sense. Rather, assignments are based on the reasonable assumption that the stereoselective behaviour of a catalyst is broadly similar for both the polymerization of symmetrical and unsymmetrical alkyl norbornene

and norbornadiene derivatives (this may not be valid for more radical variations in the structure of the monomer). The characteristics of each catalyst are then defined from studies with the optically active monomers, as described in the previous section.

An important aspect of this study, within the present context, was that the analysis of the ^{13}C n.m.r. spectra of the polymers formed yielded a wealth of microstructural information showing not only an unprecedented degree of *m/r* dyad splitting but also triad tacticity, *mm*, *mr*, *rm* and *rr*, on several of the signals; this is illustrated by the spectrum of the high *trans* atactic poly(**21**) prepared using the RuCl_3 catalyst (Figure 5a). The atactic nature of this polymer and the syndiotactic nature of the high *cis* polymer formed using the ReCl_5 catalyst (Figure 5b), where only five sharp lines are observed, are entirely consistent with the behaviour of these catalysts when used to polymerize (+)-**6**, (+)-**10** and **18**.

Polymers of intermediate *cis* content were also analysed, and the resolution was such that it was possible to determine the tacticity of both *cis* and *trans* junctions. This can be seen to great effect in the contrasting cases of polymers produced using two tungsten-based catalysts of different oxidation state and ligation, i.e. $\text{WCl}_6/\text{Bu}_4\text{Sn}$ and (mesitylene)- $\text{W}(\text{CO})_3$, and a Ru(trifluoroacetate) system with hard ligands. Figure 5c-e shows that each catalyst produces a polymer with a similar *cis/trans* ratio but distinctly different tacticity. The WCl_6 -based system (Figure 5c) produces an atactic polymer in which *cis* and *trans* double bonds are associated with both *m* and *r* dyad units, whereas a tactic polymer, *cis/r* and *trans/m* only (Figure 5d), is produced from the (mesitylene) $\text{W}(\text{CO})_3$ -based system. Figure 5e is the spectrum of an intermediate case of a semi-tactic polymer in which the Ru(trifluoroacetate) catalyst gives only *cis r* junctions, but *trans* junctions which are *m* and *r* in equal proportion. It may also be calculated from these latter spectra that there is a blocky distribution of *cis* and *trans*

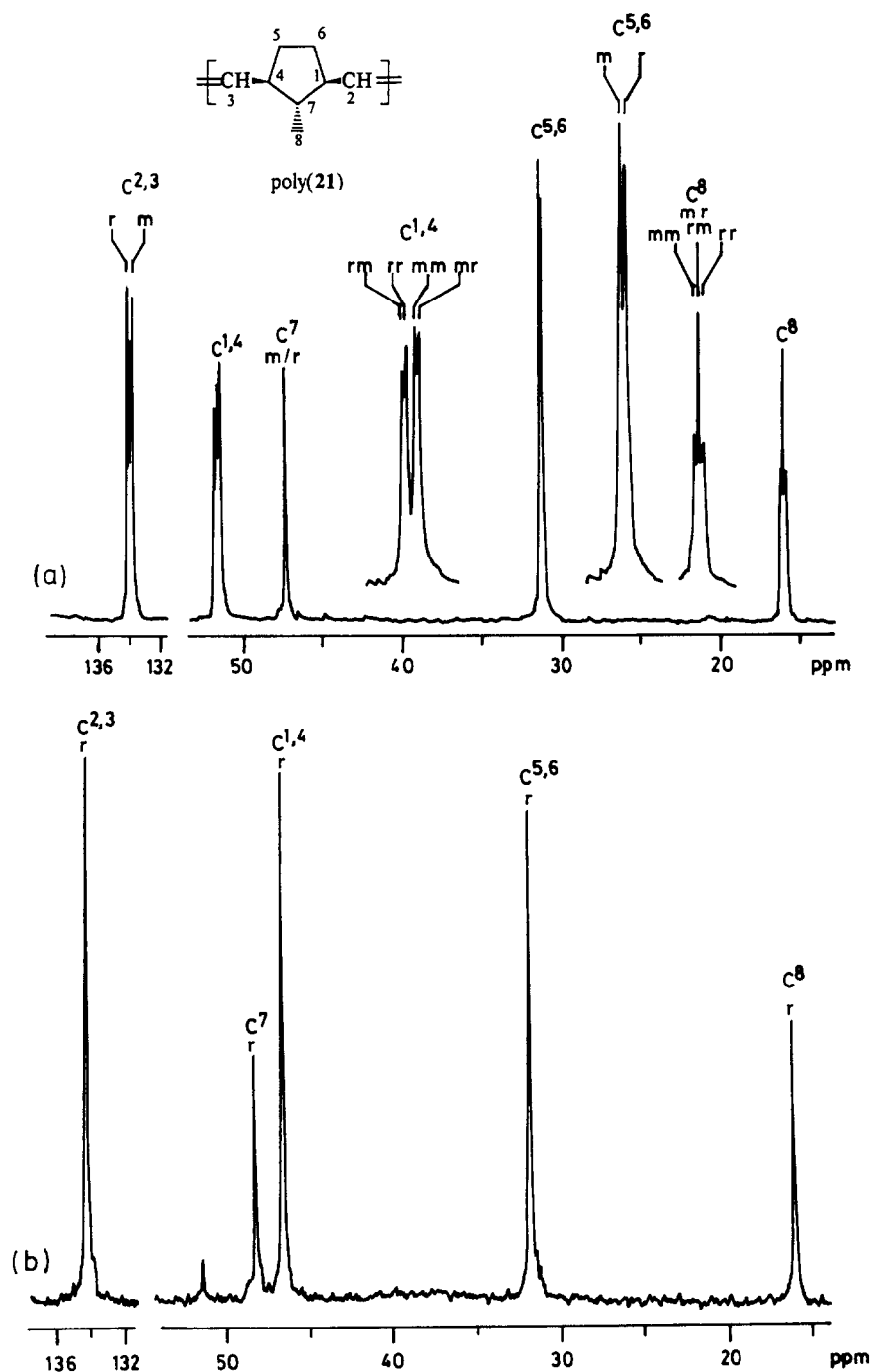


Figure 5 62.8 MHz ^{13}C n.m.r. spectra of poly(21): (a) high-*trans* atactic polymer, RuCl_3 catalyst; (b) high-*cis* syndiotactic polymer, ReCl_5 catalyst; (c) 52% *cis* atactic polymer, $\text{WCl}_6/\text{Bu}_4\text{Sn}$ catalyst; (d) 45% *cis* syndiotactic/55% *trans* isotactic polymer, (mesitylene) $\text{W}(\text{CO})_3/\text{EtAlCl}_2$ catalyst; (e) 56% *cis* syndiotactic/44% *trans* atactic polymer, $\text{Ru}(\text{TFA})$ catalyst. Reproduced from *J. Mol. Catal.*, Hamilton, J.G., Ivin, K.J. and Rooney, J.J., Microstructure and mechanism of formation of the ring-opened polymers of syn and anti-7-methylbicyclo[2.2.1]hept-2-ene initiated with metathesis catalysts, 1995, **28**, 255–278. With kind permission of Elsevier Science, Amsterdam.

double bonds which is expressed in numerical terms by the product $cc/ct \times tt/tc \approx 6$ (the notation *cc*, *ct* etc. is used to define lines and their intensity in the ^{13}C n.m.r. spectra which arise from the different arrangements of double bond pairs, the chemical shift of a given cyclopentenyl carbon being sensitive to the stereochemistry of the adjacent double bonds^{20,51}; thus $cc/ct \times tt/tc = 1.0$ quantifies a random distribution).

Both the blockiness and the tacticity observed here are in accord with the mechanism outlined earlier which views the polymerization in terms of propagation by kinetically distinct metallacarbenes, \mathbf{P}_c and \mathbf{P} , which are distinguished by the nature of the last-formed double bond. For the case of

totally tactic polymer, prepared using the (mesitylene)- $\text{W}(\text{CO})_3$ catalyst, it was envisaged that the species \mathbf{P} and \mathbf{P}_c , which are self-regenerating and as such lead to blocks of *cis* and *trans* double bonds, are responsible for the formation of *trans*(*m*) and *cis*(*r*) junctions respectively. The *cis/trans* distribution is blocky, and this leads to a stereoblocky polymer (blocks of *m* and *r* dyads) when the double bonds are removed by hydrogenation. Semi-tactic polymer, prepared using the $\text{Ru}(\text{trifluoroacetate})$ catalyst, which contains both *trans*(*r*) and *trans*(*m*) junctions, arises when the *trans* forming species \mathbf{P} is symmetrical or epimerizes at a rate which is faster than propagation. The chiral identity of \mathbf{P}_c is maintained by the coordinated *cis* double bond, leading

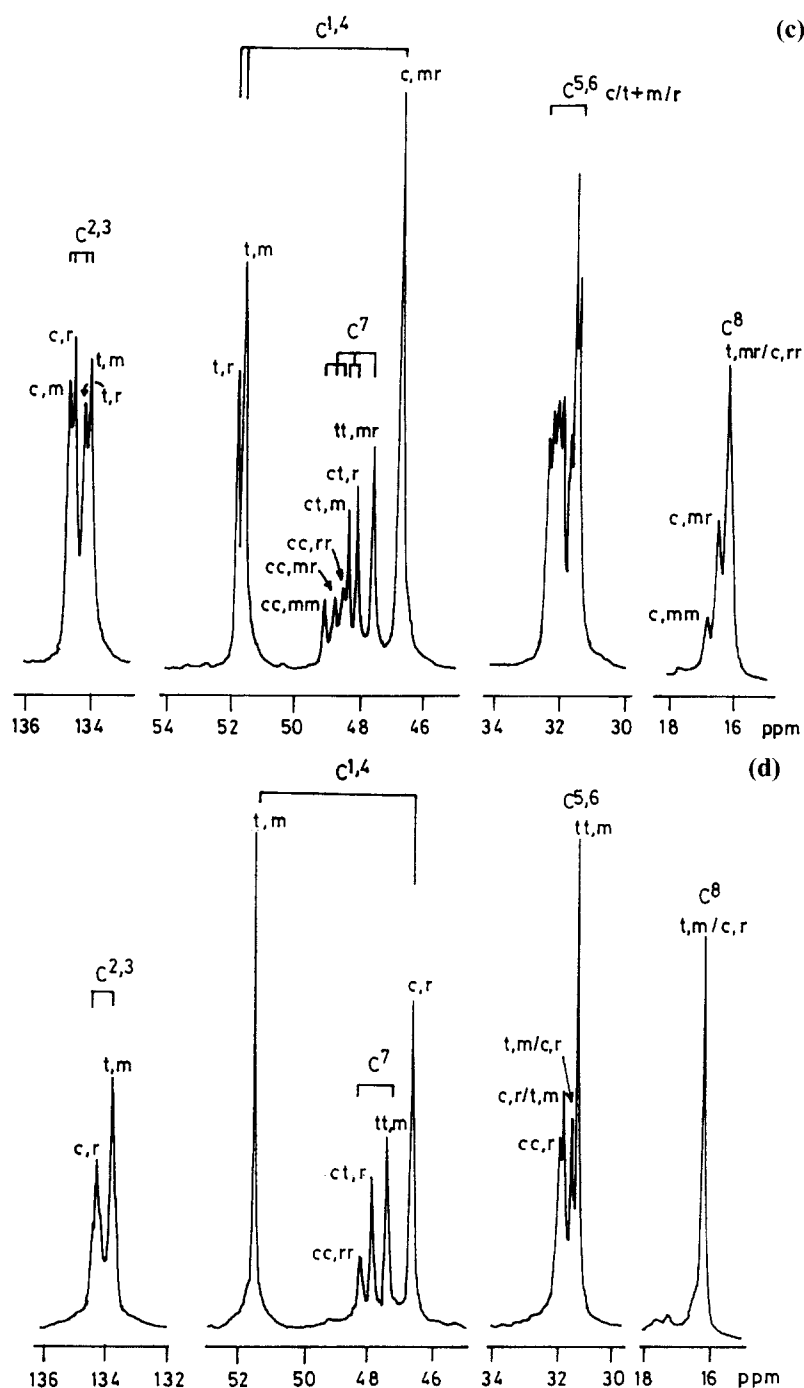


Figure 5 Continued

to the formation of only *cis*(*r*) junctions. Epimerization at the metal centre or relaxation to a different geometry of both **P** and **P**_c leads to the formation of totally atactic polymer, in which each type of junction, *cis* or *trans*, is associated with both *r* and *m* units.

Three additional features of the spectra are particularly noteworthy because they demonstrate the need for caution when interpreting the spectra of polymers if only a limited range of microstructural types are available for analysis. The quartet structure of the C2, 3 resonance in the high *trans* atactic polymer (Figure 5a) is lost in polymers which contain both *cis* and *trans* double bonds, an effect probably caused by masking by longer range *cis/trans* splitting. The methyl, C8, signal appears as a singlet in the spectrum of the *cis/trans*, tactic, polymer (Figure 5d), but as a multiplet when a polymer of the same *cis* content is atactic (Figure 5c), which means that the primary splitting arises from *m/r*

rather than *cis/trans* effects. Finally, in this atactic polymer the C7 *cc* signal is a triplet (*rr*, *mr* and *mm*) whilst the *tt* signal is not resolved; this leads to the *ct* signal appearing as a doublet because only the *cis* unit is sensitive to tacticity, so the signals are assigned *cc,mr* and *cc,rr*.

It is also interesting to note the effects that substituents with different steric requirements have on the degree of *m/r* splitting. The bulkier *anti*-7-ethyl derivative, **23**⁵², and its spiro analogue, **24**⁵³, both yield high *trans* polymers with the RuCl_3 catalyst and each shows greater *m/r* resolution than in the case of the methyl derivative. In fact the *m/r* splitting in the spectra of poly(**23**), for the sterically more demanding *cis* dyads, is up to three times greater than in the methyl case, but this is compensated by a general decrease in *m/r* splittings for *trans* dyad units; in polymers formed from **24** comparative splittings are increased for both types of dyad. Also, a recent study⁵⁴ of the hydrogenated

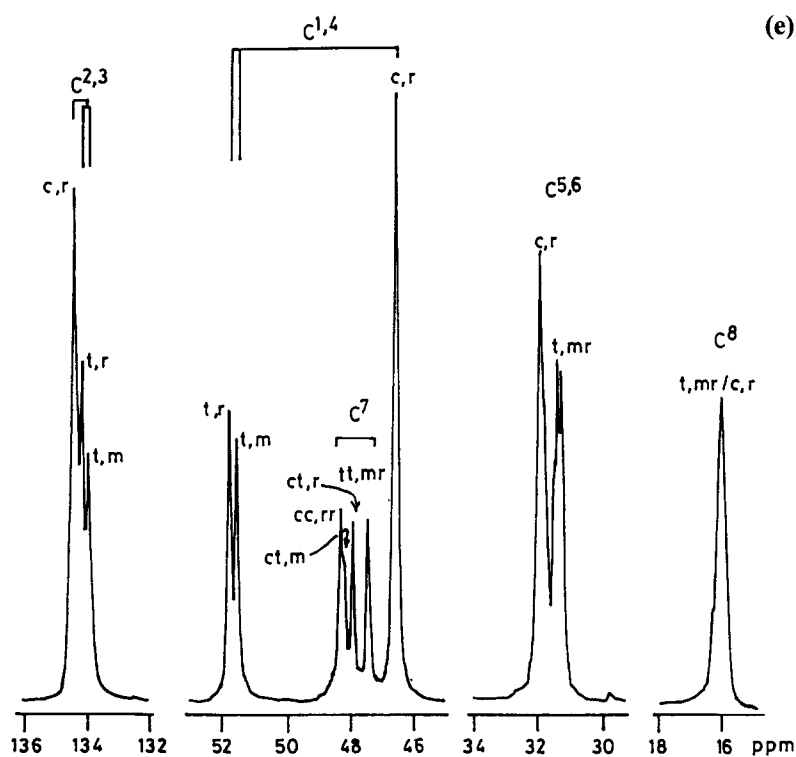


Figure 5 Continued

polymers formed from *endo*-5-methylnorbornene and **7** as well as **6** shows enhanced *m/r* splittings in the HH units relative to the TT and HT(TH) units. However, despite its novel structure the usefulness of **24**, as a tacticity diagnostic, like *exo,endo*-5,6-dimethylnorbornene, **10** (see relevant section), is limited by its inability to form even moderately high *cis* polymers, and this has been ascribed to the steric demands of the cyclopropyl ring.

Microstructural studies of polymers formed from norbornadiene are frequently hampered by their insolubility, although this difficulty has been overcome by employing chain transfer reagents such as 1-hexene which lower molecular weight. The spectra of polymers formed using this technique have shown some very interesting microstructural features; e.g., a tendency to give high *cis* materials has been noted and is believed to be the result of propagation by catalyst sites sterically crowded by the monomer molecules which also act as chelating, spectator ligands. As with poly(**2**), there are no well defined tacticity splittings in the ^{13}C n.m.r. spectra.

Polymers formed from 7-substituted norbornadienes³¹, **25** and **26**, have exhibited levels of tacticity resolution comparable to that observed in the poly(**21**) case³⁹. The appearance of the signal for the symmetrically positioned C7 carbon in the case of poly(**25**) makes an interesting comparison since, in these spectra, it is the *tt* signal which exhibits a well defined tacticity triplet whereas the *cc* signal is only poorly resolved (Figure 6a); the exact opposite holds for poly(**21**). Also, the *ct* signal appears as a quartet because now both *cis* and *trans*-centred dyads are sensitive to tacticity; the quartet is then assigned *ct,rr*; *ct,mr*; *ct,rm* and *ct,mm*. Different microstructural types of poly(**21**) formed with other catalyst systems bear out this analysis. For example, in the polymer formed using the (mesitylene)-W(CO)₃-based catalyst *cis* double bonds are associated predominantly with *r* ring dyads and *trans* with *m*, so the main *ct* signal is now *ct,rm*, the *ct,mr* signal is too small to

be observed and *cc* and *tt* signals are now represented by *cc,rr* and *tt,mm* (Figure 6b).

A qualitatively similar picture emerges from an analysis of the C8 resonance (Figure 6d), however, there is now substantial overlap due to *cis/trans* and tacticity splittings which are of the same order of magnitude. The *m/r* splitting for the *cis* signal (~0.8 ppm), Figure 6c is one of the largest ever observed for polymers based on this ring system. Polymers formed from the 7-phenyl, **26**⁵⁵, and the 7-*t*-butoxy, **27**³², derivatives have also been studied and, whilst the former show the expected tacticity splittings, the spectra for the latter are complicated by the fact that alkoxy substitution allows reaction to occur at both the *syn* and *anti* faces so that it is difficult to distinguish between splittings due to *syn* and *anti* units and those due to tacticity.

Polymers formed from 5,6-disubstituted norbornadienes

A large number of 5,6-disubstituted norbornene and norbornadiene derivatives have been polymerized by ring-opening metathesis and, in a number of these, fine structure attributable to tacticity has been observed in their ^{13}C n.m.r. spectra. Substituents in these monomers range from the simple dimethyl derivatives, **28** and **29**, through diesters, **30**, **31** and **32**, chiral versions³⁶ of which, **14** and **15**, have been considered in some detail in a previous section, to fused aromatic, **33**⁵⁵, and aliphatic, **34**⁵⁶, rings and bis-trifluoromethyl derivatives, **35**.

Recently, polymers formed from **35** have attracted much interest⁵⁷ because of their highly dipolar nature. The potential dielectric and pyroelectric properties of these materials will depend to a large extent on the ability to control the polymer microstructure, and so a number of studies have considered this problem^{23,58,59}. Although it has proved possible to exercise a reasonable degree of control over the *cis/trans* ratio using classical catalyst systems⁶⁰, the use of initiators such as **11** and **12** has allowed not only the complete control of the *cis/trans* ratio¹⁷ but also the production of polymers in

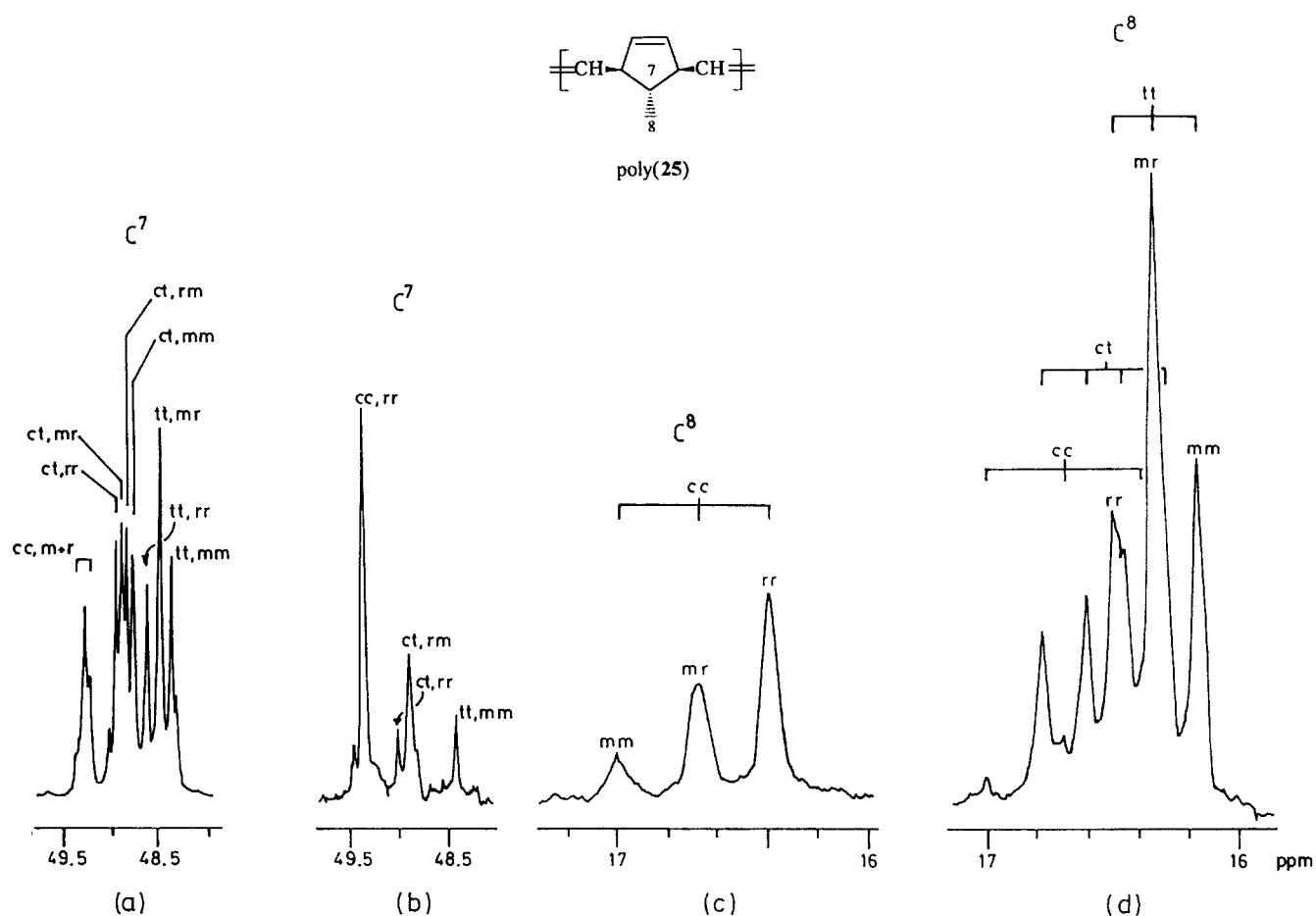
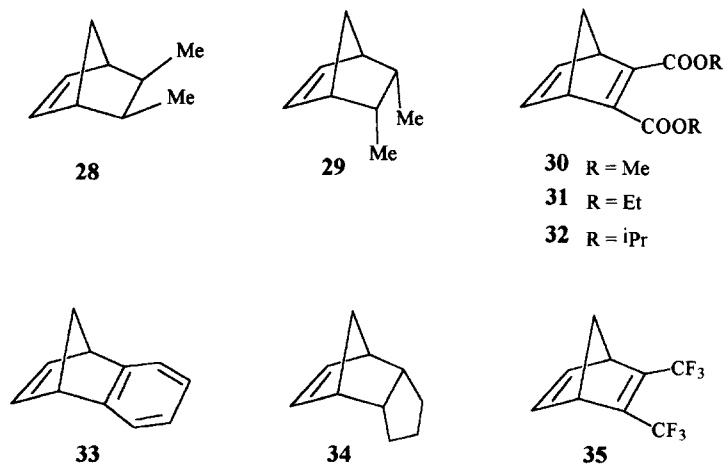


Figure 6 125 MHz ^{13}C n.m.r. spectra of poly(25): (a) the C7 signal in a 20% *cis* atactic polymer $\text{MoCl}_5/\text{Me}_4\text{Sn}/\text{Et}_2\text{O}$ catalyst; (b) the C7 signal in a 76% *cis* syndiotactic/24% *trans* isotactic polymer, $(\text{mesitylene})\text{W}(\text{CO})_3/\text{EtAlCl}_2$ catalyst; (c) the C8 signal in a 97% *cis* predominantly syndiotactic polymer, OsCl_3 catalyst; (d) the C8 signal in a 20% *cis* atactic polymer, $\text{MoCl}_5/\text{Me}_4\text{Sn}/\text{Et}_2\text{O}$ catalyst. Reproduced from Hamilton, J.G., Snowden, D.G. and Rooney, J.J., *Makromol. Chem.*, 1993, **194**, 2907, by permission of Hüthig and Wepf Publishers, Zug, Switzerland

which the tacticity may be varied from highly syndiotactic to highly isotactic, depending on the nature of the alkoxy ligand attached to the Mo centre²⁷.

The *cis/trans* double bond ratio in polymers formed from **35** is readily determined by inspection of the C1,4 region of the ^{13}C n.m.r. spectrum and, at least in high *cis* cases, further fine structure has been attributed to the effect of different tacticities²⁷. Less is known about the tacticity in high *trans* cases, and in polymers formed from **35** using MoCl_5 -based catalysts tacticity splitting is not evident in the published spectra⁶⁰, despite the fact that the polymer is probably atactic. The fact that tacticity splitting is present in the

spectra of the *cis* but may not be present in the *trans* polymer is not unexpected and may be attributed to the fact that the *cis* junctions are more sterically crowded. This may be a more general phenomenon because recently spectra have been obtained from samples of poly(**2**)⁴⁸, where, for a given carbon atom, *trans* lines are sharp but *cis* lines are considerably broader, some with incipient splitting. The methylene, C7, carbon in partially tactic high *cis* poly(**35**) (Figure 7a-c) displays the expected triplet structure, but a remarkable degree of splitting, $\delta_{mm} - \delta_{rr} = 1.9$ ppm, over twice that in any example so far reported³¹, is observed. However, as is always the case when a polymer has a



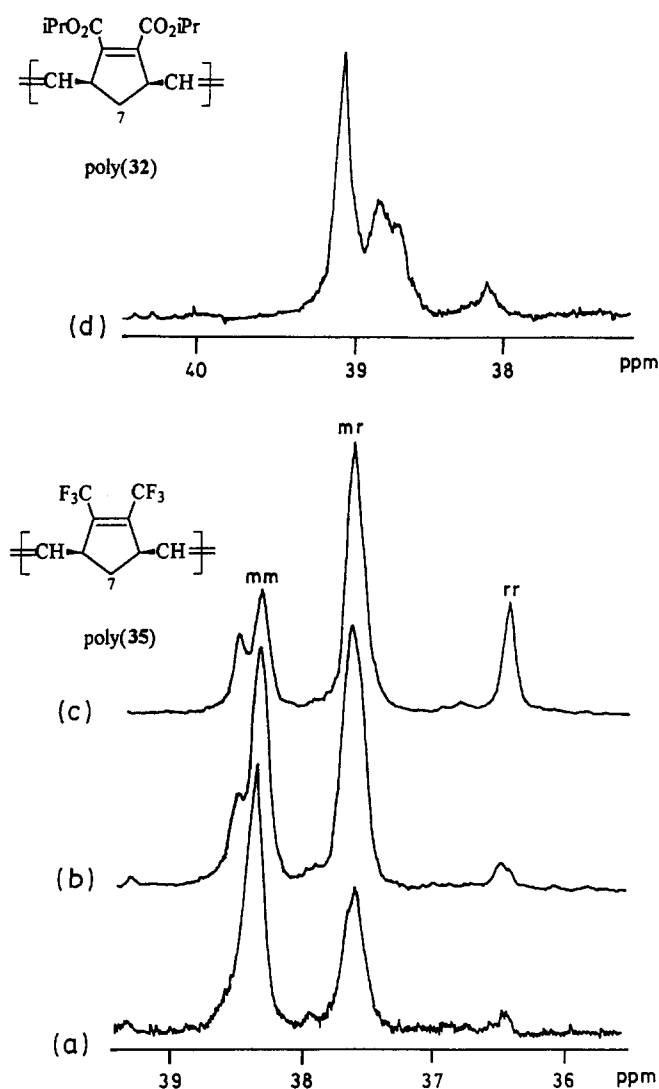


Figure 7 125 MHz ¹³C n.m.r. spectra, methylene region, of high-*cis* samples of poly(35), (a), (b), (c), and poly(32), (d), exhibiting non-symmetrical tacticity splitting with possible pentad sensitivity. Reproduced with permission from Schrock, R.R., Lee, J.-K., O'Dell, R. and Oskam, J.H., *Macromolecules*, **28**, 5933. ©1995 American Chemical Society

symmetrical repeating unit, assignment of the components of the fine structure to *m* and *r* dyads is not straightforward and one has to rely on indirect methods. In the present case assignments were made by the method, referred to earlier, of extrapolating from the known behaviour of a particular stereoselective catalyst and making the assumption that the catalyst will behave similarly with related monomers. This led to the assignment of the most downfield line to C7 in an *mm* triad and the most upfield line to C7 in an *rr* triad.

Two other features of the C7 resonance are unusual and noteworthy. Firstly, an additional signal, just downfield of the main *mm* line, appears and grows in intensity as the proportion of syndiotactic dyads increases (Figure 7a, b and c respectively), and secondly, in each example, regardless of the tacticity, the triplet is very obviously non-symmetrical, $(\delta_{mr} - \delta_{rr})/(\delta_{mm} - \delta_{mr}) \approx 1.5$. The first feature is commented upon by the authors²⁷ and is thought to be due to the effect of more remote pentad tacticity to which presumably only the C7 *mm* signal is sensitive, so the *mm* peak may now be partially resolved into *mmmm* and one of the other pentad possibilities *rmmm*, *rmnr* or *mmnr*. A similar feature is observed in the central component of the C7 line (presumed to be *mr/rm*) in the spectra of polymers formed from 32²⁷ (Figure 7d).

The fact that the C7 triplet, irrespective of the polymer tacticity, is not symmetrical is more obscure but has important implications for line assignments in general because it demonstrates that carbon atoms symmetrically positioned in repeating units need not necessarily give rise to symmetrical sets of lines in the ¹³C n.m.r. spectra. One can, for example, envisage problems arising when attempting the assignment of partially overlapping lines in polymers containing both *cis* and *trans* double bonds, and this emphasises the need to have available high *cis* and high *trans* samples. This line asymmetry may be a more general feature and is obvious in a number of cases where the *mr* splitting is sufficiently large, for example, in the spectra of polymers formed from diesters, 31 and 32, and also to a lesser extent in the *cis* C7 resonance in poly(21)³⁹. It is also analogous to the unsymmetrical set of lines observed in the spectra of numerous high-*cis* poly(2) where the splitting pattern of the minority *trans*-centred double bond triads is also unsymmetrical and believed to arise as a result of a conformational stress arising from the occurrence of *trans* units in high *cis* chains¹¹.

Earlier studies by Feast *et al.*⁵⁹ on the polymerization of 35 using related catalysts produced high *cis* and high *trans* polymers which were also believed to be highly tactic. Here the tacticity was assessed by a novel method, applicable to polymers containing highly dipolar repeating units, of measuring the relaxed dielectric constants at temperatures above *T_g*. It was found that whilst a 98% *trans* sample had an ϵ_R value of 40, the 54% *trans* and the 2% *trans* polymers had significantly lower values of 15 and 6 respectively. Of the two types of tacticity possible for the high *trans* sample only a syndiotactic structure could possess a sufficient number of cooperatively aligned dipoles to give this high value. The low ϵ_R value for the high *cis* polymer, however, is more ambiguous because, as the authors point out, the polymer may adopt a number of possible conformations in which the cooperativity of the dipoles would cancel and therefore these low values do not necessarily indicate a *cis* syndiotactic structure; such a structure should, however, give low values for ϵ_R because neighbouring dipoles, being oriented in different directions, will cancel. In fact, inspection of the ¹³C n.m.r. spectra of polymers produced under very similar conditions in a more recent study²⁷ shows that these high *cis* materials range from essentially atactic to moderately isotactic, which is consistent with the results of the dielectric constant study.

HYDROGENATED POLYMERS

A number of metathesis polymers have been shown to undergo rapid and quantitative hydrogenation in the presence of diimine, generated *in situ*⁶¹, provided that the basic requirement of polymer solubility is met.

Although this reagent had been used to hydrogenate polymers formed by other routes, its first application to ROMP was the determination of tacticity of samples of poly(18), described earlier⁴³. Since then, however, this general hydrogenation technique has found several applications^{31,35,39,52,55,56,62-64} and it is now clear that a study of the ¹³C n.m.r. spectra of the hydrogenated derivatives of any new metathesis polymer is an important aspect of characterization.

This diimine hydrogenation method is vastly superior to catalytic methods⁶⁵ and is highly selective in that polar double bonds and aromatic rings are inert⁶²; also, it has been demonstrated recently that HH units in polymers formed

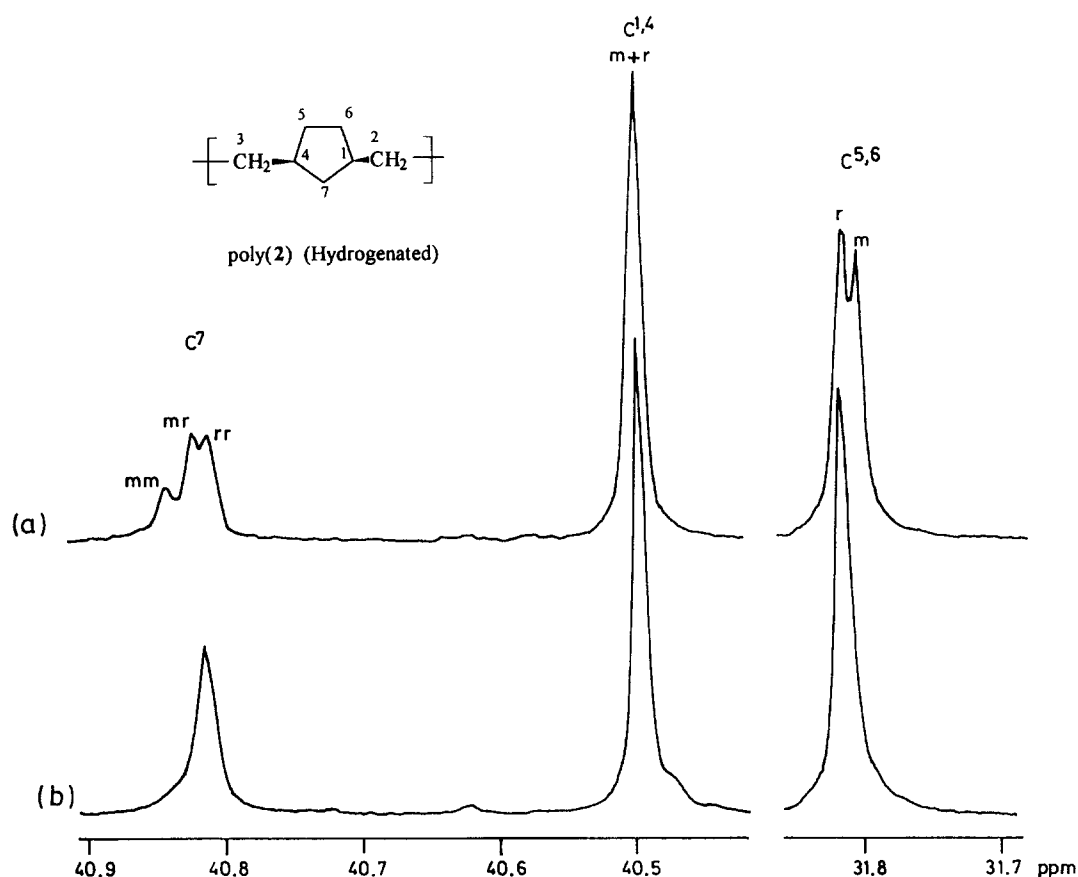


Figure 8 125 MHz ^{13}C n.m.r. spectra of hydrogenated poly(2): (a) essentially atactic polymer with a small syndiotactic excess; (b) a highly syndiotactic polymer. Reproduced from Al-Samak, B., Amir-Ebrahimi, V., Carvill, A.G., Hamilton, J.G. and Rooney, J.J. *Polymer International*, 1996, **41**, 85 with permission from the Society of Chemical Industry

from **6** are reluctant to react⁵⁴, so steric as well as electronic factors are important. These hydrogenated polymers, although only poorly swollen in chloroform at room temperature, give clear solutions at 50° and analyses of several of the high quality ^{13}C n.m.r. spectra thus obtained have been reported. The spectra, if measured on suitably dilute samples, generally show well resolved fine structure which, at least in the case of symmetrical monomers, where there is no fine structure due to different substituent orientations, must necessarily be due to tacticity. In numerous cases these splittings are not present in the spectra of the parent polymer.

The tacticity of the hydrogenated polymers is directly related to that of the parent polymer because the relative configuration of the chiral carbon atoms, C1 and C4, in the main chain is established during the ring-opening polymerization process and is unaffected by hydrogenation. The method is particularly suited to the determination of tacticity because other potential methods of main chain modification such as bromination or epoxidation, apart from complications due to double bond isomerism, introduce new chiral centres which will yield more complex spectra. An exception to this, however, is deuteration, which may be carried out using the readily prepared deuterated form of the reagent, thus enabling one to identify previously unsaturated carbon atoms; this is essential for preliminary assignments of spectral lines⁴³.

Ideally, the method is suited to high *cis* or high *trans* polymers and becomes rather ambiguous when intermediate *cis/trans* materials are analysed. This arises because it would be impossible to distinguish between (a) polymers in which *cis* and *trans* double bonds are associated only with syndiotactic and isotactic dyads respectively, i.e. tactic

polymer, and (b) atactic polymers in which no such correlation exists. However, this apparent restriction of the methodology is now perhaps of less importance because many of the potentially more interesting, preformed metallocarbene initiators, as described herein, are quite stereoselective with respect to *cis* and *trans* double bond formation.

Perhaps one of the most useful developments of this methodology was the observation of fine structure in the spectra of hydrogenated samples of polymers formed from norbornene, poly(2)⁶⁶. Unlike all other monomers used in the determination of tacticity, **2** is both readily available and highly reactive and therefore the behaviour of even the least active catalyst system may be investigated. Norbornadiene, arguably more reactive, suffers from the disadvantage of a limited *cis/trans* ratio range in the polymers, which also have a strong tendency to become insoluble through crosslinking. However, in suitable cases soluble samples of both these polymers may be hydrogenated to chemically identical materials, so the behaviour of catalysts in the polymerization of these archetypal monoene and diene monomers may be compared directly.

The spectra of hydrogenated samples of poly(2), measured under optimal conditions, comprise four lines, two of which, the C7 line and the C5,6 line, are sensitive to tacticity and appear as a doublet and triplet respectively. This is illustrated by examples of a highly syndiotactic polymer, *Figure 8b*, and an essentially atactic polymer but with a small syndiotactic bias, *Figure 8a*. An important practical consideration is that, because of the very small differences in chemical shift of the *m* and *r* lines, one cannot effectively distinguish between highly syndiotactic and highly isotactic polymers taken in isolation. It is necessary

therefore to examine the spectra of carefully prepared mixtures of tactic and atactic polymers; comparison of the line intensity ratios in the various samples then allows a distinction to be made.

CONCLUSION

The polymerization of various norbornene-based monomers using a range of ROMP catalysts and their subsequent analysis, primarily by ^{13}C n.m.r. spectroscopy, has led to the establishment of a general methodology whereby the tacticity of polymers produced by many such catalyst/monomer combinations may be assessed. In cases where the monomer is available in chiral form, polymer tacticity may be established unambiguously.

Currently, detailed information on the tacticity of ROMP polymers is restricted to those formed from monomers based on the norbornene ring system, but it is envisaged that the techniques described herein will be applied successfully to other structural classes, with particular effect where the monomer is chiral and available in resolved form.

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