

# Dramatic solvent effects on ring-opening metathesis polymerization of cycloalkenes

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## Abstract

A series of metathesis polymers and copolymers have been formed and their structures were analysed by <sup>13</sup>C NMR spectroscopy. Noble metal and non-noble metal salt catalysts are distinguished by their behaviour in various solvents. Thus, in phenolic solvents, the former class produce alternating copolymers from cyclopentene and norbornene, while the latter are unaffected and produce random copolymers. In contrast, ether solvents have the effect of markedly increasing the *cis* content of polymers from the latter catalysts while the former are unaffected.

The tacticity of various polymers are correlated through their hydrogenated derivatives and found to depend on the type of monomer as well as the catalysts. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Metathesis polymers; Alternating copolymers; Acidic alcohols and ether solvents; Tacticity; <sup>13</sup>C NMR

## 1. Introduction

Detailed studies, using <sup>13</sup>C NMR spectroscopy, on the microstructures of numerous ROMP polymers and copolymers have led to the development of theories, which provide a rationalization of the polymer's primary microstructural features, e.g., *cis/trans* double bond ratio and distribution, regiochemistry, copolymer ratios and tacticity [1].

Many of these studies have been carried out using the classical metal salt-type catalysts with several of these being identified as 'cornerstones' because they have consistently produced

polymers with specific microstructures such as all *cis* and syndiotactic. In addition, a library of monomers has now been assembled, which allows the different characteristics of a given catalyst, in terms of its potential for stereospecific polymerization and selectivity in copolymerization, to be ascertained [2].

Recent studies using acidic alcohols, phenols, and ethers as solvents have revealed dramatic effects. Thus, alternating copolymerization of norbornene (NBE) and cyclopentene (CPE) is achieved when dry phenols and acidic alcohols are used with noble metal halide catalysts [3]; the reasons for this remarkable result have been further investigated and are now reported. Also, ether solvents, used with non-noble metal halide catalysts, have had the effect of raising the *cis*

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content of many polymers to almost 100% and this has been exploited in terms of tacticity determination. Our results are now described, especially for the important prototype monomers, NBE and norbornadiene.

## 2. Experimental

### 2.1. Materials and instrumentation

GPR grade solvents were used throughout the study. Dioxan was distilled from  $\text{CaH}_2$ , chlorobenzene and phenol were distilled from  $\text{P}_2\text{O}_5$  before use. The metal salts  $\text{OsCl}_3$  (Acros),  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{ReCl}_5$ ,  $\text{WCl}_6$ ,  $\text{MoCl}_5$ ,  $\text{TaCl}_5$ ,  $\text{NbCl}_5$  and the cocatalysts  $\text{Me}_4\text{Sn}$  and phenylacetylene (all from Aldrich) were used as received.

The monomers, NBE, norbornadiene and CPE (Aldrich) were distilled from  $\text{CaH}_2$  before use. 5,6-Exo-(dicarbomethoxy)norbornene [4], 5,6-dicarbomethoxynorbornadiene [5], 7-methylnorbornene [6], 7-methylnorbornadiene [7], 5,5-dimethylnorbornene [8] and 1-methyl-norbornene [9] were synthesized by methods previously described.

$^{13}\text{C}\{^1\text{H}\}$  NMR spectra were obtained at 75.45 MHz on a Bruker Avanc DPX 300 spectrometer, and polymer samples were dissolved in  $\text{CDCl}_3$  with TMS as an internal standard.

### 2.2. Polymerization procedures

Polymers were prepared according to the procedures outlined below. Although dry solvents were used, no particular attempt was made to carry out the reactions anaerobically. In each case, polymers were recovered by precipitation in methanol followed by washing with methanol and vacuum drying.

#### 2.2.1. Alternating copolymerization of CPE and NBE

Catalyst systems were prepared by adding 2 g dry phenol to commercial samples of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  or  $\text{OsCl}_3$  (8 mg) contained in plastic-

capped sample bottles. A mixture of CPE (1.7 g, 24 mmol) and NBE (0.3 gm, 3 mmol) was then added and the reaction mixture kept at room temperature overnight. Polymer was recovered by dissolving the gel in chloroform followed by precipitation in methanol and vacuum drying to yield typically 240 mg copolymer,  $M_w$   $1.3 \times 10^6$  (polystyrene standards). When other dry phenolic solvents such as *p*-chloro and *p*-fluorophenol, as well as trifluoroethanol are used in the same manner, alternating copolymers are also produced.

Addition of one or two drops of water to the above reactions at the start results in the production of random copolymer.

#### 2.2.2. Non-noble metal catalysts ( $\text{MCl}_x / \text{Me}_4\text{Sn}$ ) in dioxan solvent

The metal halide (100 mg) was added to dioxan (1.5 ml) followed by tetramethyl tin (four drops). After a 2-min induction at  $20^\circ\text{C}$ , the monomer (500 mg), dissolved in dioxan (1.5 ml), was added and reaction was allowed to proceed for 24 h at room temperature. In the case of polymers formed from 5,5-dimethylnorbornene, a solvent mixture of chlorobenzene (4 ml) and dioxan (0.7 ml) was used.

#### 2.2.3. Preparation of hydrogenated polymers

Typically, ring-opened polymer (100 mg) was dissolved in xylene (10 ml) and *p*-toluenesulphonhydrazide (2 g) was added, the solution was stirred with heating at  $120^\circ\text{C}$  for 2 h [10]. After cooling, the reaction mixture was poured into methanol (50 ml) and the precipitated polymer, after several washings with methanol, was retrieved by filtration or centrifugation as appropriate.

## 3. Results and discussion

### 3.1. Alternating copolymerization

Copolymerization of pairs of monomers, which differ in reactivity, followed by  $^{13}\text{C}$  NMR

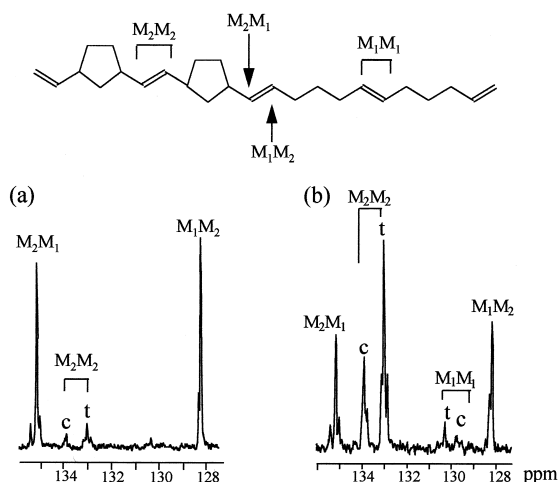


Fig. 1.  $^{13}\text{C}$  NMR spectra of copolymers of norbornene ( $\text{M}_2$ ) and cyclopentene ( $\text{M}_1$ ); (a) alternating copolymer formed using the  $\text{RuCl}_3$ /phenol catalyst, (b) random copolymer formed when a small amount of water is added to the  $\text{RuCl}_3$ /phenol catalyst.

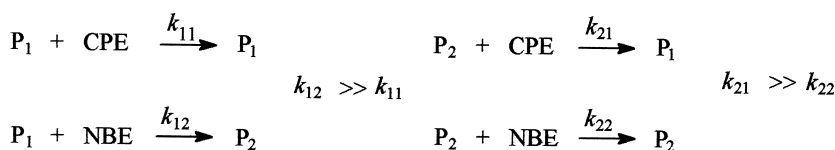
analysis of the composition of the product formed at low yield, is an excellent method of assessing the relative reactivity of different catalysts; with very reactive catalysts the copolymer composition tends to reflect the monomer feed ratio while less reactive catalysts are more discriminating with respect to the more reactive monomer. In a number of cases, notably the CPE/NBE system, one may determine not only the copolymer composition but also the distribution of monomer units along the chain, merely by inspection of the copolymer's  $^{13}\text{C}$  NMR spectrum [11].

Using such methods, we examined the behaviour of various classical catalyst systems in unconventional solvents such as ethers, alcohols and phenols in order to determine the effect of the different solvents on catalyst activity and on

the stereochemical course of the reaction. It was noted that with halide catalysts derived from W, Mo and Ta, ether solvents, which can coordinate to the metal centre, had the effect of increasing *cis* selectivity, *vide supra*, with a predictable decrease in catalyst activity, while dry phenolic solvents had little influence.

The most novel results, however, were obtained with the noble metal catalysts derived from  $\text{RuCl}_3$  and  $\text{OsCl}_3$  in phenolic solvents. These salts, used conventionally in ethanol/chlorobenzene solvent mixtures, have only moderate to low reactivity as judged by the above criteria and yield high *trans* copolymers with a random, or rather blocky, distribution of NBE and CPE units. In dry phenolic solvents however catalyst activity increases and the distribution of repeating units is highly alternating, as is shown by the relative intensity of the  $\text{M}_1\text{M}_2/\text{M}_1\text{M}_1$  and  $\text{M}_2\text{M}_1/\text{M}_2\text{M}_2$  signals in the polymers  $^{13}\text{C}$  NMR spectrum, Fig. 1(a).

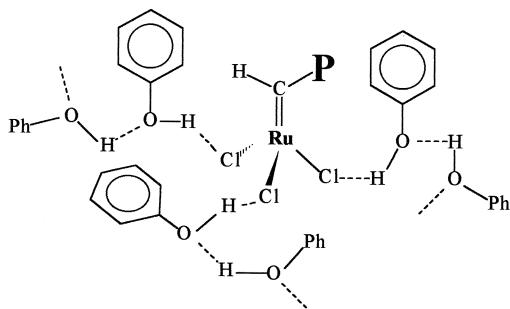
Although the kinetics of this reaction may be described in terms of the conventional copolymerization equations, Scheme 1, where  $k_{12} \gg k_{11}$  and  $k_{21} \gg k_{22}$  (1 = CPE and 2 = NBE), it was not at first apparent why the chain carriers,  $\text{P}_{\text{NBE}}$  and  $\text{P}_{\text{CPE}}$ , were so different. A vital clue was provided by the fact that we initially observed substantial variations in the degree of alternation when damp phenolic solvent was used, whereas use of rigorously dried solvent consistently gave highly alternating copolymer. Indeed, small quantities of water added to these dry reactions gave copolymers with random distributions, Fig. 1(b). These observations suggest that hydrogen bonding between the solvent and the catalyst site is important and a working hypothesis is that propagation is occurring at a



Scheme 1.

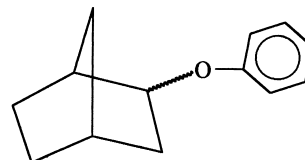
site sterically constrained by a hydrogen bonded solvent cage.

We originally believed that the site was based on a Ru[phenoxide] species with additional phenol molecules attached through the medium of hydrogen bonding, however, microanalysis of samples of RuCl<sub>3</sub>, which had been subjected to several cycles of heating with dry phenol, followed by complete removal of the solvent under high vacuum, had approximately the same chlorine content as the original sample (42.88% before treatment, cf. 42.25% after treatment). This evidence, and the fact that it has recently been recognized that halogen atoms bound to metals can act as hydrogen-bond acceptors [12,13], has led us to postulate a catalyst site based on RuCl<sub>3</sub> with phenol molecules hydrogen bonded to the chloride ligands as depicted by structure 1.



Alternating copolymerization then occurs at this site because the differences in steric properties and reactivities, not only of the monomers but of the chain ends that they form, are now greatly emphasized by the presence of the cage or cryptand-like pocket formed by the solvent. In this model, Scheme 2, the site formed after NBE has reacted is too constrained to allow another NBE access so the smaller CPE reacts; now the site is less constrained and although both NBE and CPE have access the more reactive NBE reacts, completing the cycle. Under the same conditions, IrCl<sub>3</sub> behaves in a similar fashion to RuCl<sub>3</sub> but to our surprise OsCl<sub>3</sub> yielded a homopolymer of CPE, the less reac-

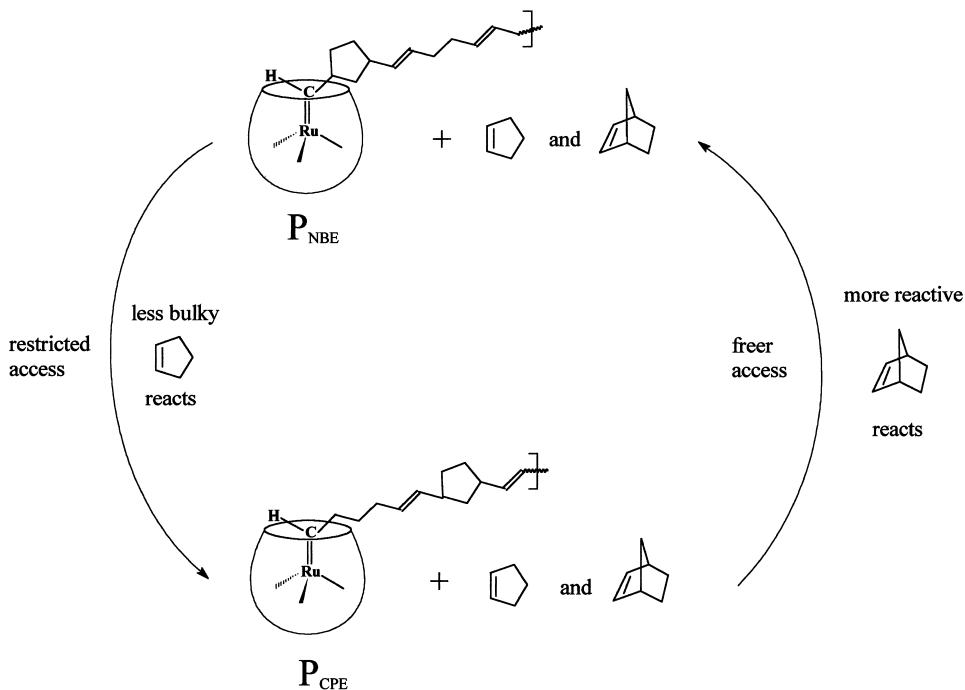
tive monomer. This apparently anomalous result may at first sight be explained by the fact that substantial quantities of the norbornyl ether, **2**,



are formed in this reaction, apparently removing much of the NBE from the reaction mixture. Conversely however, we believe that the formation of this ether is then promoted because the solvent cage effect operates here in a more extreme form with the OsCl<sub>3</sub> catalyst, now  $k_{22} = k_{12} \approx 0$  (Scheme 1) such that NBE access is essentially zero; under these conditions NBE is then available for the alternative process of ether, **2**, formation. This is supported by the fact that in a series of polymerizations where phenol is increasingly diluted with chlorobenzene, monomer and catalyst concentrations being held constant, only small increases in NBE incorporation in the copolymer are observed even though there is progressively less opportunity for ether formation as the phenol concentration falls. In fact, as long as dry conditions are maintained, one may use very dilute solutions of phenol in chlorobenzene and still maintain the alternating architecture, with both RuCl<sub>3</sub> and OsCl<sub>3</sub> catalysts. This discovery, that reagent quantities of phenol are as effective as neat phenol, is important and is the subject of current studies.

### 3.2. Tacticity

The first serious attempts to determine the absolute tacticity of ROMP polymers was made in the early 1980s when unsymmetrically substituted NBEs, e.g. 5,5-dimethyl [8] and later, 5,6-dimethyl [14] derivatives were resolved into their enantiomers, which were then polymer-



Scheme 2.

ized. In the resulting materials, the type of tacticity is manifest as an orientational bias of substituents along the polymer chain. Thus with the former monomer syndiotactic (r) polymers have a head-to-head/tail-to-tail bias and isotactic (m) polymers a head-to-tail bias; the degree of bias, and hence tacticity, is readily determined by  $^{13}\text{C}$  NMR spectroscopy, especially of the olefinic carbon atoms. Any head-to-tail bias arising from inherent regioselectivity was easily checked by polymerizing the racemic monomers. In fact, with the above monomers the substituents are remote from the double bond, essentially no inherent head-to-tail bias is ever observed, so they act merely as labels. When the substituents are closer, e.g. at the 1-position as in 1-methylnorbornene inherent head-to-tail bias is noted with a variety of catalysts when using racemic monomer, so the method of absolute tacticity determination based on monomer resolution cannot be used in such cases [2].

An early work [15] had shown that for the prototype polymers, poly(norbornene) and

poly(norbornadiene), many  $^{13}\text{C}$  NMR lines were well split by *cis/trans* effects but that there was no m/r resolution. On the other hand, the polymers made from the analogously symmetrical anti-7-methylnorbornene [6] and anti-7-methylnorbornadiene [7] showed several  $^{13}\text{C}$  NMR lines very well resolved by m and r effects on both *cis* and *trans* signals. Tacticity assignments were made on the basis of the behaviour of certain 'cornerstone' catalysts, e.g.  $\text{ReCl}_5$  and  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$ , which with resolved 5,5- and 5,6-dimethyl norbornenes, gave very high *cis*, syndiotactic polymers [8,14]. Where symmetrical monomers, such as 7-methylnorbornene, also gave high *cis* tactic polymers, it was assumed that these were also syndiotactic. However, we were uneasy about the universal application of these assumptions as indications appeared in the overall body of the research that, apart from the nature of the catalyst, small changes in monomer structure could also profoundly effect tacticities, thus, in recent years we have sought to develop methods which will

lead to more confident assignment of tacticities for all metathesis polymers.

In many cases, hydrogenation gives identical, fully-saturated polymers from different but related precursor polymers, e.g. poly(norbornene)/poly(norbornadiene), poly(7-methylnorbornene)/poly(7-methyl-norbornadiene) and poly(5,6-dioxocarbomethoxy-norbornene)/poly(5,6-dicarbomethoxy-norboradiene). On hydrogenation the *cis/trans* level of complexity is removed and m/r splitting, if it occurs, is self evident. For each catalyst, the corresponding  $^{13}\text{C}$  NMR microstructural features of the three materials, polyene, polydiene and polyane, can then be compared. This approach is also greatly facilitated if one can start with all-*trans* or all-*cis* polyene and polydiene because the complexities arising from *cis/trans* effects are then eliminated. To this end, the use of ether solvents with non-noble metal catalysts has turned out to be greatly advantageous in this respect as *cis* content is often raised to  $\approx 100\%$ .

High *cis* (> 90%) poly(norbornene) was obtained using several catalysts;  $\text{ReCl}_5$  in chlorobenzene,  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$  in chlorobenzene/ethanol, and  $\text{WCl}_6$ ,  $\text{MoCl}_5$ ,  $\text{NbCl}_5$  and  $\text{TaCl}_5$ , with  $\text{SnMe}_4$  cocatalyst in dioxan; in chlorobenzene solvent the *cis* content of the polymers is  $\leq 50\%$  when using these very reactive non-noble metal halides with  $\text{SnMe}_4$  as cocatalyst. When the samples were hydrogenated, the  $^{13}\text{C}$  NMR spectrum revealed that the poly(norbornane) obtained using all the latter catalysts was atactic whereas when the catalyst was  $\text{ReCl}_5$  or  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$ , it was totally tactic, presumably syndiotactic on the basis of the behaviour already stated for these latter catalysts, *vide supra*. The m/r resolved lines, a  $\text{C}^7$  (triplet) and a  $\text{C}^2$  (doublet), were, therefore, assigned respectively as  $\delta_{\text{mm}} < \delta_{\text{mr}} = \delta_{\text{mm}} < \delta_{\text{r}}$ , and  $\delta_{\text{m}} < \delta_{\text{r}}$  [10].

Now that we are more confident of this assignment, we looked at the  $^{13}\text{C}$  spectra of the poly(norbornene) precursors in greater detail. Two hitherto unrecognised features concerning tacticity were discerned, as shown in Fig. 2. The

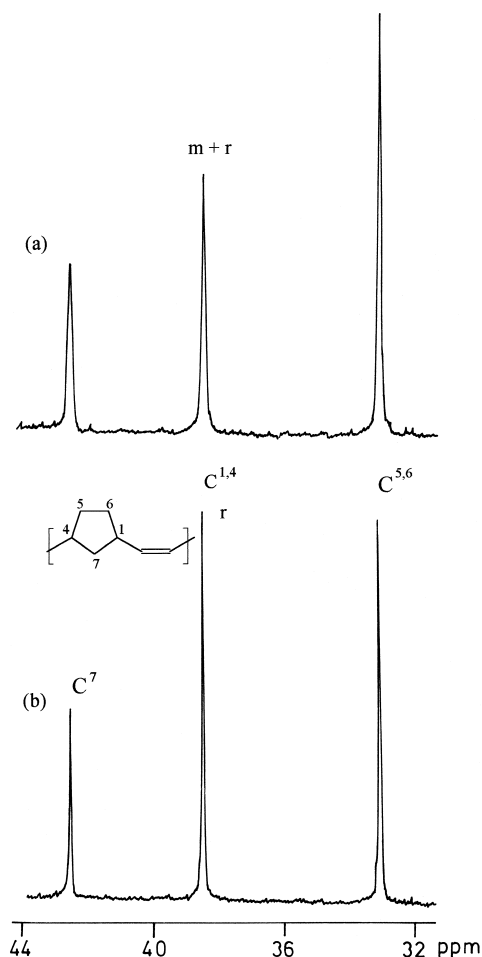


Fig. 2.  $^{13}\text{C}$  NMR spectra of poly(norbornene), cyclopentyl region; (a) atactic polymer prepared using the  $\text{WCl}_6/\text{Me}_4\text{Sn}$  catalyst in dioxan solvent; (b) syndiotactic polymer prepared using the  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$  catalyst in dichloromethane solvent.

$\text{C}^{1,4}$  line for the atactic sample, Fig. 2(a), is half the height and twice the width of the  $\text{C}^{5,6}$  line, but of equal height and width for the syndiotactic polymer, Fig. 2(b). The incipient m/r splitting (seen by the relative peak heights) is therefore a measure of the tacticity.

A distinction between the syndiotactic and atactic polymer is also apparent when the *trans* olefinic region of the spectra of these materials is examined, Fig. 3. In polymers believed to be syndiotactic, the  $\text{C}^{2,3}$  line is resolved into a triplet *ctt*, *ttt* + *ctc* and *rtc*, Fig. 3(a), but in the

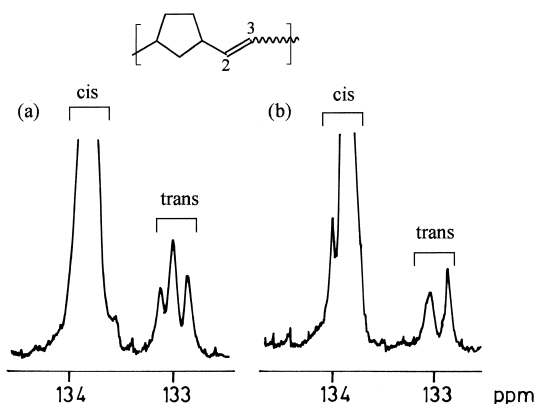


Fig. 3.  $^{13}\text{C}$  NMR spectra of poly(norbornene), olefinic region; (a) syndiotactic polymer prepared using  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$  catalyst in dichloromethane solvent; (b) atactic polymer prepared using the  $\text{WCl}_6/\text{Me}_4\text{Sn}$  catalyst in dioxan solvent.

atactic cases the *m* content of the polymer has apparently caused a shift of the *ctt* line such that only a doublet appears with the *ctt* line now underneath the *ttt* + *ctc* line, Fig. 3(b).

Poly(norbornadiene) exactly parallels poly(norbornene) in that tacticities were not assignable for the former but can be discerned for the fully hydrogenated material, the poly(alkane) [10]. With this in mind all-*cis* polymers were again prepared using the  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$  catalyst, and the  $\text{MoCl}_5$ ,  $\text{WCl}_6$ ,  $\text{TaCl}_5$ , and  $\text{NbCl}_5$ -based catalysts in dioxan; again, hydrogenation revealed that the poly(alkane) from the noble metal salt was totally syndiotactic whereas the others were atactic.

When the  $^{13}\text{C}$  NMR of the poly(norbornadiene) samples themselves were now closely examined the  $\text{C}^{5,6}$  (olefinic resonance) appeared as a single (*r*) line for the syndiotactic producing  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$  catalyst, Fig. 4(a), but as a well-defined doublet (*m/r*) for all the others, e.g. Fig. 4(b) and (c). The analysis and consistency of these checks allows us to be confident of the tacticity assignments.

High *cis* poly(5,5-dimethylnorbornene) was then made using  $\text{MoCl}_5$  and  $\text{WCl}_6$  with  $\text{SnMe}_4$  in dioxan. When these samples were analysed both showed the usual head-to-tail (HT), tail-

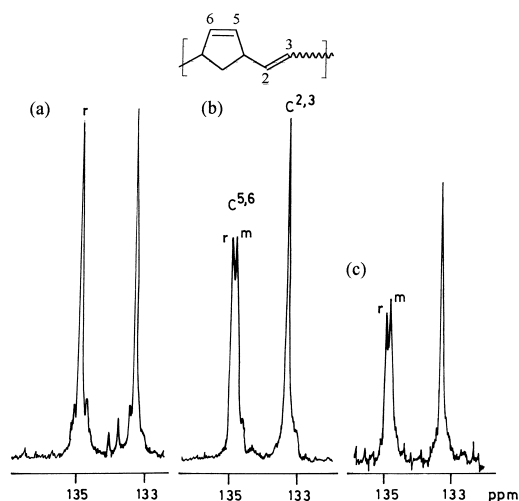


Fig. 4.  $^{13}\text{C}$  NMR spectra of poly(norbornadiene), olefinic region; syndiotactic polymer prepared using  $\text{OsCl}_3/\text{PhC}\equiv\text{CH}$  catalyst in dichloromethane solvent; (b) atactic polymer prepared using the  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  catalyst in dioxan solvent; (c) atactic polymer prepared using the  $\text{NbCl}_5/\text{Me}_4\text{Sn}$  catalyst in dioxan solvent.

to-tail (TT), head-to-head (HH) and tail-to-head (TH) lines for the  $\text{C}^{2,3}$  olefinic carbon atoms and the HH line was resolved (*m/r*), Fig. 5, as it is for all *trans* polymers made using  $\text{RuCl}_3$  as catalyst [8]. Hydrogenation of this polymer and

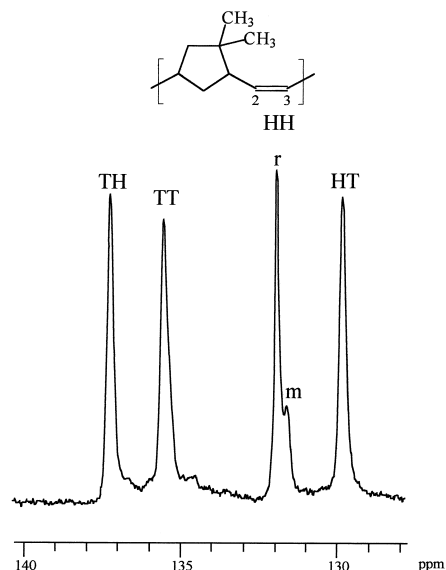


Fig. 5.  $^{13}\text{C}$  NMR spectrum, olefinic region, of poly(5,5-dimethylnorbornene) with a strong syndiotactic bias.

comparison with other such materials of varying tacticities [16] revealed that it was  $\sim 70\%$  syndiotactic (HH line), a surprising contrast to the atactic character of poly(norbornadiene) and poly(norbornene) made using the same initiators; this is another indication that tacticity may also be highly monomer dependent.

Another interesting aspect is that while many NBEs and norbornadienes, monosubstituted, or disubstituted in the 5 and 6 positions give higher *cis* polymers using dioxan as solvent with the Lewis acidic non-noble metal halides, this is not the case for 1-methylnorbornene where the substituent is closer to the double bond. Here, although again dioxan greatly reduces the rate of polymerization the *cis* content is the same as in chlorobenzene solvent. Obviously there is an equilibrium,  $P + S = PS$ , where P is the propagating species, S the solvent, and PS the solvent bound metal complex. When the methyl substituent is closer to the double bond, as in 1-methyl-norbornene, only the unsolvated form of the chain carrier, P, can propagate, giving the normal higher *trans* polymer; PS is too sterically crowded to permit metallacycle formation.

When copolymerization of NBE and CPE is attempted using these very high *cis* directing catalysts in dioxan, hardly any CPE is incorporated, which shows that the strain energy of CPE in comparison to that of NBE is not sufficient to permit the former to enter into metallacyclobutane formation at the sterically crowded (PS) propagating site. This behaviour is quite distinct from that of the noble metal salts in phenolic solvents where the *cis* content is unaffected and both NBE and CPE enter the polymer chain. We believe this to be due to the manner in which the solvent interacts at the catalyst site. With the non-noble metals, ether solvent is coordinated directly at the strongly Lewis acidic metal centre and steric compression dictates the type of metallacycle, *cis* or *trans*, which can form. This is analogous to the effect of chelating diolefins, which act as spectator ligands during their polymerization with  $\text{OsCl}_3$  and  $\text{RuCl}_3$ , which leads to the formation

of high *cis* polymers [17,18]. When phenolic solvents are used with these latter metals, the solvent is not coordinated directly at the metal centre but at the chloride ligands where it can influence the choice of monomer entering the cage but is not close enough to the metal to dictate the type of metallacycle that may form.

#### 4. Conclusion

When solvents complex to the active species, which propagate the metathesis reaction, either via hydrogen bonding from acidic alcohols and phenols to halide ligands, or via Lewis acid/Lewis base interaction of ethers with acidic non-noble metal salts, dramatic changes in the microstructures of the metathesis polymers and copolymers are observed. With a given catalyst, the tacticity of the ROMP product may also be dependent on the monomer structure and care must be taken when extrapolating the behaviour of one monomer to another for a given catalyst.

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