Copolymerization of cycloalkenes as a probe of the propagation steps in olefin metathesis

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Abstract

A range of ring-opened metathesis copolymers of norbornene and cyclopentene have been prepared and ^{13}C NMR spectroscopy used to analyse in detail the nature of the homo and heterodyad units. This has provided significant new information on the sensitivity of the [2 + 2] cycloaddition step in metathesis to the steric and electronic factors associated with the [Mt]=C and C=C moieties involved. Novel very high *cis* directing catalyst systems, have also been developed for the homopolymerization of norbornene using various ethers with Mo and W-based catalyst systems or chelating dienes and phenylacetylene with $RuCl_3$ and $OsCl_3$ systems. The general feature of *cis/trans* blockiness at high *cis* content is investigated in much greater detail. A clearer description of the associated relaxation processes of the propagating species emerges from this work. The metathesis polymerization of the matched pair, benzonorbornadiene and 7-oxa-benzonorbornadiene has been investigated using Ru and Os-based initiators. The results illustrate the subtle way whereby the presence of the proximate 7-O-atom may facilitate [2 + 2] cycloadditions. This constitutes a valuable novel method of studying key electronic factors in the mechanism of the metathesis reaction.

Keywords: Cycloalkene copolymerization; Ruthenium; Osmium

1. Introduction

Olefin metathesis is known to be a member of a family of metal catalysed reactions, beginning with the discovery of Ziegler–Natta addition polymerization, all of which involve [2 + 2] cycloadditions and reversals as the key mechanistic steps.

The metal alkyl propagating species for the Ziegler–Natta sub-group may involve an α-agostic H atom [1] and is thus carbenoid in character, while true metallacarbenes are at the centre of the metathesis polymerization of cy-

cloalkenes and acetylenes [2]. Since metal–carbon π-bonds are present the elementary mechanistic steps shown are therefore members of the general class of $[2\pi + 2\pi]$ reactions, which are known to be very sensitive to electronic and steric factors associated with the participating π-partners. We can therefore expect that the ring-opening metathesis polymerization (ROMP) of cycloalkenes will also be sensitive in the same fashion to similar factors for both moieties, metallacarbene and cycloalkene respectively, in these cycloaddition and cycloreversion steps.
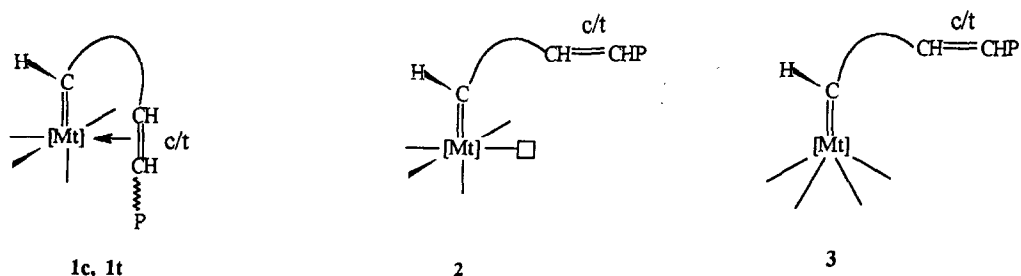
The purpose of this work is to show that such steric and electronic factors can be studied conveniently by way of copolymerization of differ-
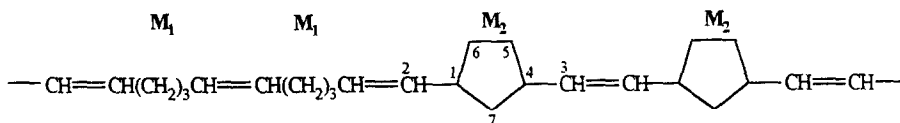
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ent cycloalkenes, using NMR spectroscopy to determine the structural features of dyads and triads. This permits us to characterize in detail the successive Tolman or catalytic cycles in the overall chain reaction. We have already shown [3] that there are two types of *cis* and *trans* double bond blockiness in the homopolymers of norbornene in the higher *cis* materials. There is thus a tendency for the *trans* units to occur in pairs, i.e. –cccttcccc–, or in t_n blocks ($n > 2$) for noble metal catalysts. Such blockiness can be described as a tendency to form *cis* after *cis* and *trans* after *trans*, and is reminiscent of the stereoselectivities often observed in the metathesis of 2-alkenes, e.g. pent-2-enes, where there is a tendency to form *cis* products, e.g. but-2-ene and hex-3-ene, from *cis* starting materials, and *trans* products from *trans* starting materials [4]. The blockiness in the ROMP of NBE clearly indicates that two or more kinetically distinct metallacarbene propagating species are involved [2]. We have explained this by assuming that each Tolman cycle is not necessarily complete before the next successive one commences, with the result that there is an information relay factor operating, which increases the probability of *cis* after *cis* and *trans* after *trans* formation beyond the random distribution. The first product from the $[2\pi + 2\pi]$ cycloreversion is an olefin-metallacarbene, **1**, whose character is determined by the nature of the stereochemistry of the last-formed olefinic unit (*cis* or *trans*). If **1** propagates before the last formed double bond leaves the coordination

sphere of the metal it is already kinetically distinguished (*cis* or *trans*). Furthermore, a *trans* unit may leave more readily than a *cis* unit such that **2**, and the more relaxed form, **3**, are the predominant species after a *trans* event, whereas, **1** is the main propagating species after the formation of a *cis* unit. Concomitant relaxation processes on going from an *n*-fold to an $(n - 1)$-fold coordinated species are also likely, which will also alter the reactivity and stereochemistry of the metallacarbene (Scheme 1). Distinct differences in electronic and steric features are therefore readily envisaged, so we have suggested that **1c**, because of steric compression, tends to make another *cis* unit whereas, **2** and especially **3** are highly *trans* directing [3]. Stereoselective influences such as these are expected to be multiplied when we come to copolymers such as that of NBE and cyclopentene (CPE = M₁). Now we can examine the detailed structures of M_1M_1, M_2M_2 and M_1M_2 units, **4**, together with compositional blockiness and competition ratios, as well as *cis/trans* blockiness (Scheme 2). So far there has been very little work done in this area, with only copolymers of NBE and CPE being studied in depth [5] for one very reactive catalyst system which gave essentially random *cis/trans* and M_1/M_2 compositions. The homodyads, M_2M_2, had $\sigma_c \approx 0.5$ (σ_c = the fraction of *cis* units) which is indicative of a very reactive nondiscriminating propagating species.

Recently we have found a variety of convenient catalyst systems which afford very high

Scheme 1.

$$\mathbf{M_1} \quad\quad \mathbf{M_1} \quad\quad\quad \mathbf{M_2} \quad\quad\quad \mathbf{M_2}$$

—CH=CH(CH₂)₃CH=CH(CH₂)₃CH=CH—⟨⟩—CH=CH—⟨⟩—CH=CH—

4

Scheme 2.

2. Experimental, results and discussion

2.1. Copolymers of norbornene and cyclopentene

In spite of the fact that NBE is more bulky than CPE it is much more reactive in copolymerization, the higher strain energy in NBE rendering its double bond (*exo* face) far more reactive in [2 + 2] cycloadditions, etc. Thus it is essential to use a large molar excess of CPE in order to achieve significant incorporation at low conversion in copolymers with NBE.

A typical reaction mixture therefore consisted of 0.25 g NBE (0.0027 mol) and 4 cm³ CPE (0.054 mol) in 2 cm³ chlorobenzene solvent

cis homopolymers of NBE. The noble metal complexes, especially of Ru, promote high *trans* polymer formation [6]. However, when chelating agents, for example, norbornadiene [7], *endo*-dicyclopentadiene [6], benzoquinone or phenylacetylene are added, *vide infra*, exceptionally high *cis* polymers may be obtained. On the other hand we have noted [8] that the presence of Michael acceptors, such as acrylate and fumarate esters, with Mo and W–halide systems induce these very active catalysts to become high *cis* directing. Dioxan, tetrahydrofuran and other ethers, including polyethers, also have the same effect [9]. We therefore decided to investigate further the copolymers of NBE and CPE deliberately using these new high *cis* and the high *trans* directing catalysts, in order to probe the steric and electronic factors involved in propagation at these extremes.

added to a solution of 30 mg RuCl₃ · 3H₂O in 2 cm³ ethanol in a Carius tube which was then sealed and left at 60°C for 24 h. The reaction was then stopped, the precipitated polymer dissolved in chloroform and reprecipitated in methanol (yield 0.10 g). The ¹³C NMR spectrum for the olefinic region is shown in Fig. 1a. ¹³C NMR spectra were recorded at 125 MHz using a GE, GN Omega 500 spectrometer.

Fig. 1b shows a comparable spectrum of copolymer made using a MoCl₅-based catalyst modified by addition of ethyl acrylate (EA) [8]. Here a mixture of 0.25 g NBE with 4 cm³ CPE and 4.9 cm³ EA was added neat at room temperature to a solution of 50 mg MoCl₅ in 2 cm³ chlorobenzene to which 10 μl diethyl ether and 0.1 cm³ tetramethyl tin had been added. After 1 h a chloroform solution of the polymer was reprecipitated as before in methanol (yield 0.55 g).

All the resonances in the homodyads, M_1M_1 and M_2M_2 are the same as those assigned previously in detail for the homopolymers [10]. The RuCl₃ initiated copolymer is high *trans* in M_2M_2 ($\sigma_c = 0.10$) whereas, the MoCl₅ catalyst system produces a polymer which is high *cis* in M_2M_2 ($\sigma_c = 0.75$). Furthermore the M_2M_2 units in the latter exhibit the typical blockiness expected of high *cis* NBE polymer made using Mo and W-based catalysts (the *trans* ctt and ttc peaks being larger than the central ctc plus ttt peak which is indicative of tt pair formation). Complete assignment of the resonances for the heterodyads M_1M_2 and M_2M_1 was possible since we have made a high-*trans* alternating copolymer of NBE and CPE using an OsCl₃ catalyst modified with *p*-benzoquinone *vide in-*
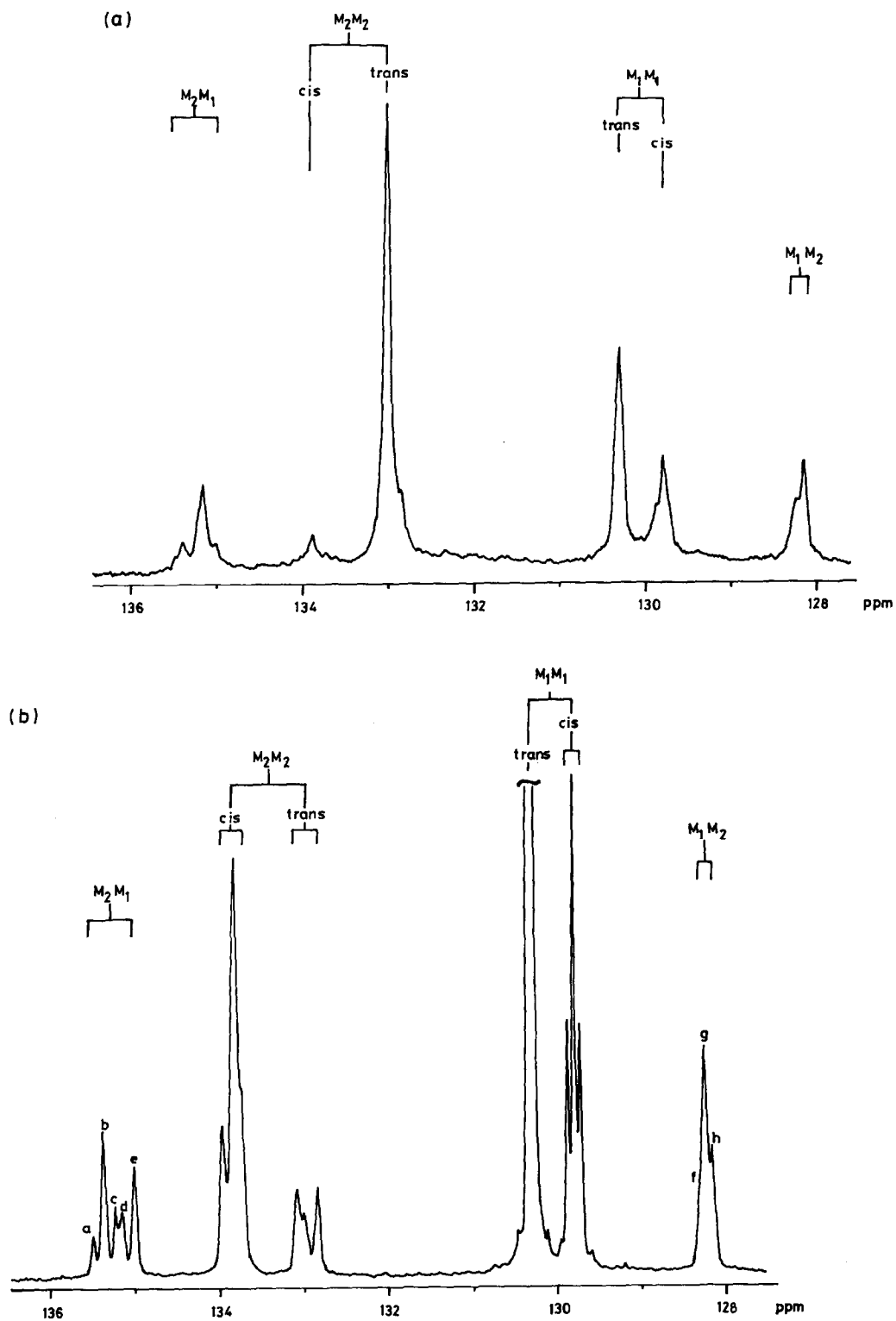
Fig. 1. Olefinic region of the ^{13}C NMR spectrum of copolymers prepared from cyclopentene, (M_1), and norbornene, (M_2), using (a) $RuCl_3.3H_2O$ and (b) $MoCl_5/Me_4Sn/Et_2O/ethyl$ acrylate, as catalyst.

fra. These resonances are labelled **a** to **h** in Fig. 1b, and the structures responsible are given in Scheme 3.

The most remarkable feature of Fig. 1a and 1b is that while $\sigma_c(M_2M_2)$ is small and large respectively, $\sigma_c(M_1M_1)$ varies little, and in both cases is intermediate, but < 0.5. Furthermore, homopolymer of NBE is induced to become
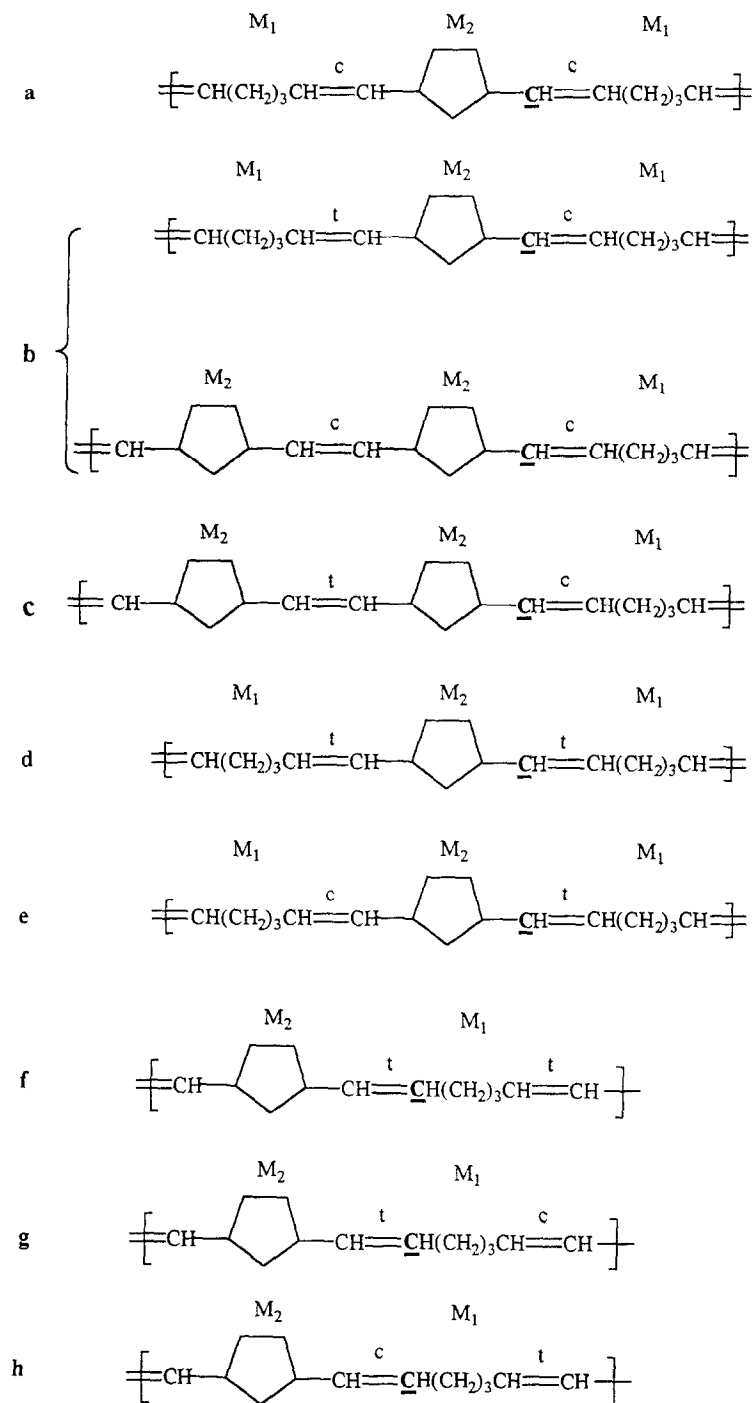

Scheme 3.

high *cis* when EA is added to the $MoCl_5$ catalyst whereas, EA has no effect on the *cis* content of homopolymers of CPE made using the same catalyst. The presence of EA results only in a decrease of the rate of reaction of CPE. The σ_c values for the M_2M_1 dyads have intermediate values between $\sigma_c(M_1M_1)$ and $\sigma_c(M_2M_2)$.

The polymers are also compositionally blocky [2] as measured by the quotients for the peak integrals,

$$\frac{\Sigma M_1 M_1 \times \Sigma M_2 M_2}{\Sigma \underline{M}_1 M_2 \times \Sigma \underline{M}_2 M_1}$$

which gave values of 15.9 for $MoCl_5$ and 9.2 for $RuCl_3$ based systems. This quotient is analogous to that estimated from the $C^{5,6}$ resonances in NBE homopolymers, $(tt/tc)(cc/ct) = r_t r_c$, which gives a measure of *cis/trans* blockiness [2].

Although NBE is much more reactive (the competition ratios are quite high in its favour [5]) the most sensitive [2 + 2] reaction sterically is clearly the following, irrespective of whether the propagating species is best represented as **1c** or **3**, see Introduction.

$$1c(M_2) + M_2 \rightarrow M_2M_2(cis)$$

$$3(M_2) + M_2 \rightarrow M_2M_2(trans)$$
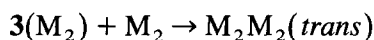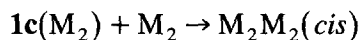
$$(M_2) = \text{Last incorporated unit}$$

The much more reactive M_2 in spite of its steric bulk is capable of reacting with $1c(M_2)$ even though steric compression forces the resulting M_2M_2 dyad to be largely *cis*. Conversely, when $3(M_2)$ is an important carrier, as for $RuCl_3$ catalysts, the steric bulk of M_2 renders metallacycle formation largely *trans*, the major factor being avoidance of vicinal *cis* substituent repulsion in the [2 + 2] cycloaddition step. Metallacycle formation involving CPE is much less sensitive to such steric factors even though CPE is electronically far less reactive. Furthermore, the fact that $\sigma_c(M_1M_2)$ is < 0.5 indicates that the carriers $1c(M_2)$ and $1c(M_1)$ are not very effective at metallacycle formation with M_1. This also accords with the fact that EA

has no effect on $\sigma_c(M_1M_1)$ in contrast to its marked influence on $\sigma_c(M_2M_2)$. This shows that when EA is coordinated to the metal the metallacarbene can react with M_2 but not with M_1.

The compositional blockiness observed in both cases may be explained if it is assumed that the propagating species $1c(M_2)$ and $3(M_2)$ are rendered even more sensitive to the electronic factor in assisting [2 + 2] cycloadditions because of the adverse steric factors mentioned. Consequently their preference for reaction with M_2 is increased over that obtaining when $1c(M_1)$ and $3(M_1)$ are the chain carriers. When $\sigma_c \approx 0.5$ for all the copolymer units, there is essentially no steric factor involved in directing the orientation *cis* or *trans* of the [2 + 2] cycloaddition steps, so the copolymers are compositionally random [2].

2.2. Cis / trans blockiness in homopolymers of norbornene

In order to achieve very high *cis* homopolymers of NBE the following experiments were carried out. A mixture of 0.3 g NBE (0.032 mol) and 0.1 g purified *p*-benzoquinone (0.0009 mol) in 2 cm^3 chlorobenzene was added to a solution of $OsCl_3$ (30 mg) in 2 cm^3 ethanol in a sealed Carius tube which was then kept at 60°C for 72 h. The usual work-up afforded polymer (yield = 0.20 g) and its spectrum for the olefinic region is shown in Fig. 2a. The value of σ_c = 0.95 is very high and the polymer is extremely blocky, $r_t r_c$ = 82, with the *trans* junctions occurring in blocks t_n ($n \geq 2$) (c.f. the resonances for M_2M_2 *trans* in Fig. 1b). The most striking feature is that the ctt peak is much lower in intensity than the ttc peak even though both represent the same *trans* unit and thus the same double bond. The two carbon atoms in question are only distinguished by the fact that the ctt olefinic carbon atom is closer to the *cis* olefinic unit.

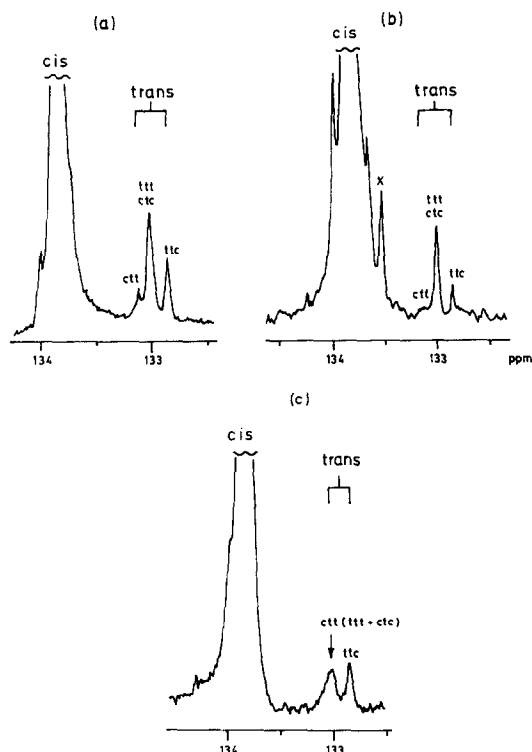This behaviour is even more dramatically observed for polymers made using $OsCl_3$ modi-

Fig. 2. Olefinic region of the ^{13}C NMR spectrum of homopolymers of norbornene prepared using (a) $OsCl_3$/p-benzoquinone ($\sigma_c = 0.95$, $r_t r_c = 82$) and (b) $OsCl_3$/phenylacetylene ($\sigma_c = 0.98$, $r_t r_c = 140$) as catalyst (the signal marked $\times$ derives from phenylacetylene) (c) (mesityl)$W(CO)_3$/EtAlCl$_2$/dioxan ($\sigma_c = 0.95$, $r_t r_c = 48$).

fied by phenylacetylene as catalyst (Fig. 2b) where the ctt peak effectively disappears. The blockiness ($r_t r_c = 140$ with $r_c = 70$, and $r_t = 2$) has now reached the highest value ever recorded; the cis content is also extremely high at $\sigma_c = 0.98$. This polymer was made by reacting 0.5 g NBE in 1 cm^3 tetrahydrofuran with 15 mg $OsCl_3$ and 100 mg phenylacetylene in 3 cm^3 dry tetrahydrofuran at 25°C followed by the usual work-up (yield 0.08 g). These $OsCl_3$ initiated high-cis polymers on hydrogenation were found to be > 90% syndiotatic [11].

Fig. 2 shows quite clearly that a sudden, partial, or whole displacement of the ctt peak must be occurring when a trans junction is incorporated after a critical high number (~ 10–20) of cis units have formed consecutively. The peak suffers a displacement to the position

of the (ctc + ttt) peak and this has just been confirmed by making very high cis polymer of NBE using the very active normally high trans directing catalyst (mesityl)$W(CO)_3$/EtAlCl$_2$ in dry dioxan as solvent. Now the tt units occur in pairs ($r_t = 1$, $r_c = 48$, $\sigma_c = 0.95$) and the ctt peak is equal in intensity to the ttc peak but has shifted to the position of the (ctc + ttt) peak, Fig. 2c. We believe that this type of peak displacement when there is an abrupt microchange or aberration in an otherwise very stereoregular polymer is due to a sudden conformational stress and may be a much more general phenomenon. A recent example is where four peaks and not simply three due to mm, m/r, and rr splitting of the C^7 resonance in some all-cis polynorbornadienes have been recorded (m = meso and r = racemic) [12].

2.3. Inverted cis/trans blockiness in norbornene homopolymers

One of the major pieces of evidence for relaxation steps of the type 1c → 2 → 3 between propagation steps is that the cis content of NBE polymers decreases dramatically on dilution of the reaction mixture [13]. This is readily understood since relaxation is first order in [1c], but propagation is also first order in [M] as well as first order in [1c] at high dilution [13]; therefore, under these conditions, according to the ideas expressed in the Introduction, more trans directing behaviour should then be noted.

We therefore decided to make NBE polymers using $OsCl_3$ under dilute conditions in order to study the effect of relaxation. The reactions were carried out in the presence of p-benzoquinone so as to maintain a sufficient cis content. In a typical experiment 0.5 g NBE and 0.38 g benzoquinone in 8 cm^3 chlorobenzene were added to a solution of 20 mg $OsCl_3$ in 8 cm^3 ethanol in a Carius tube which was then kept at 60°C for 60 h. The ^{13}C NMR of the isolated polymer (0.25 g) is reproduced in Fig. 3, ($\sigma_c = 0.31$). The C^7 cc resonance is of very low intensity and this is also reflected in the
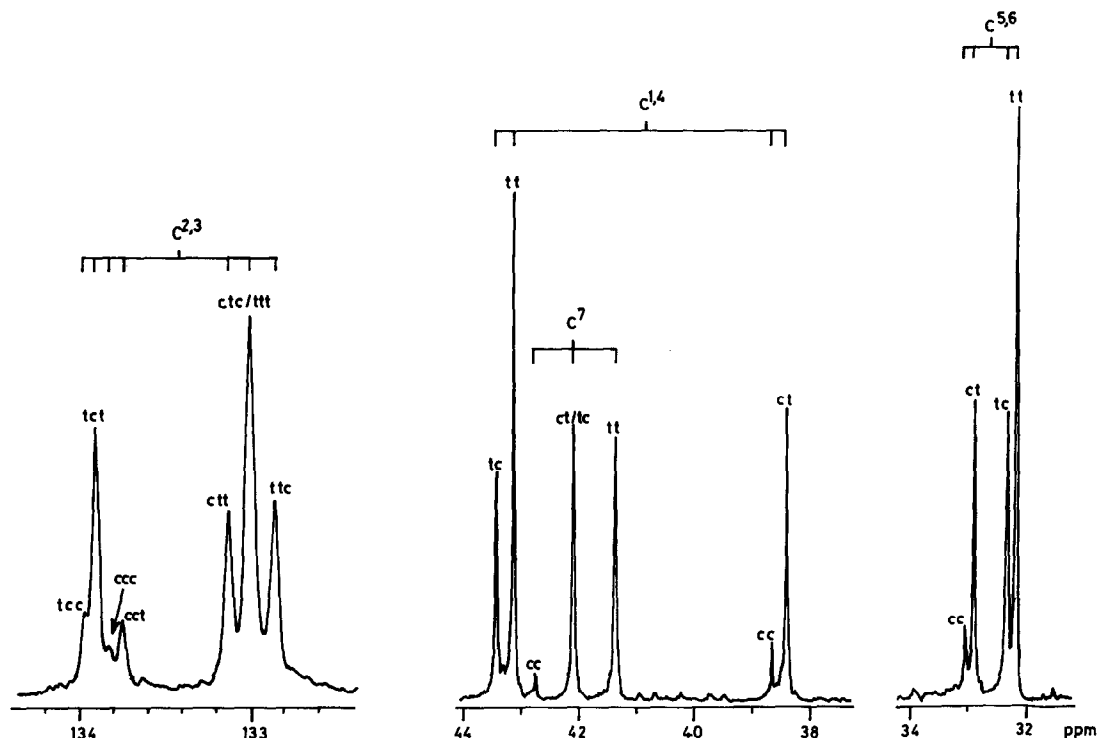
Fig. 3. ^{13}C NMR spectrum of a homopolymer of norbornene ($\sigma_c = 0.31$, $r_t r_c = 0.5$) prepared under dilute conditions and using OsCl$_3$/p-benzoquinone as catalyst.

very small ccc peak for $C^{2,3}$. The $r_t r_c$ value is 0.5, as deduced from the $C^{5,6}$ resonances, where the cc peak is also very small; this is also matched by the very small cc resonance for the $C^{1,4}$ atoms. This is the first time that we have observed an $r_t r_c$ value significantly less than unity. It shows that *cis* junctions are mainly isolated among *trans* units, since the tendency to form *cis* after *trans* is now stronger than the tendency to form *trans* after *trans*. Under dilute conditions **1c** apparently does not propagate since it has adequate time to relax. However, the relaxation process is not simply sequential **1c** → **2** → **3**, but proceeds directly from **1** to **3**, and this is more significant for **1c** to **3** than **1t** to **3**; this suggestion is based on the idea that **3** is the most highly *trans* directing species. Quite clearly relaxation in geometery of the Os-carbene complex occurs simultaneously with decoordination of the last formed *cis* unit. The presence of benzoquinone then induces the nor-

mally very high *trans* directing species **3** to become significantly more *cis* directing.

2.4. Copolymerization of matched pairs of monomers

The ROMP of 7-*t*-butoxynorbornadiene shows the surprising result that for several catalyst systems, especially Mo-based ones, there is little or no *syn/anti* discrimination in the orientation of monomer insertion into the polymer chain [14], even though the *syn-exo* face orientation should be strongly disfavoured on steric grounds. This is confirmed by the observation that there is a strong bias in favour of the *anti* orientation in the ROMP of the corresponding 7-methylnorbornadiene using the same catalyst [15]. The O atom, which is proximate to the *syn* double bond in the 7-*t*-butoxy derivative must therefore facilitate *syn* [2 + 2] cycloaddition in spite of the adverse steric factor. This is consis-

tent with the observation that benzyne preferentially adds, in a [2 + 2] reaction, at the *syn* rather than the *anti exo* face of the same substrate [16].

With this in mind we decided to investigate the role of an oxygen atom proximate to the monomer double bond by copolymerizing 7-oxa and 7-methylene norbornenes and norbornadienes, which are exactly matched in every other aspect of structure. Here we report briefly some results using 7-oxa-benzonorbornadiene and benzonorbornadiene. In a typical reaction 0.5 g of an equimolar mixture of the monomers in 1.5 cm^3 chlorobenzene was reacted with 20 mg of either $OsCl_3$ or $RuCl_3 \cdot 3H_2O$ in 1.5 cm^3 ethanol at 70°C. The reaction was stopped when it was judged that a sufficiently large sample for ^{13}C NMR analysis had formed. In both cases the yield of polymer was ~ 8%.

The fact that genuine copolymers had formed was evidenced by the ^{13}C NMR spectra as signals typical of hetero dyad units were observed; the copolymer composition was readily determined by integration of the respective groups of signals. A largely *cis* polymer (σ_c = 0.66 for both 7-oxa and 7-methylene units) with a 1:1 composition was obtained using $OsCl_3$ as catalyst. In contrast a largely *trans* material (σ_c = 0.31 for both 7-oxa and 7-methylene units) was recovered using the $RuCl_3 \cdot 3H_2O$ catalyst, but in this case the composition ratio was 5:1 in favour of the 7-oxa monomer. The proximate O atom is therefore facilitating preferential 7-oxa monomer insertion in the higher *trans* directing systems but not with the largely *cis* directing $OsCl_3$ initiator. This can be understood in terms of the *syn* lone pair on the 7-O atom engaging the C=C π-bond thereby helping to diminish the overlap of the p_π orbitals in an orthogonal approach of the [Mt]=C and C=C moieties. A weakening and polarization of the C=C π-bond in this fashion will facilitate [2 + 2] cycloadditions and such an influence due to the presence of the O-atom has been suggested to occur during the benzyne *syn* [2 + 2] cycloaddition to 7-*t*-butoxynorbornadiene [16]. The orthogonal

approach of monomer is believed to occur also with the propagating species 3 ($RuCl_3$) which is mainly responsible for the largely *trans* polymer; but for the *cis* directing system ($OsCl_3$), where propagation is mainly by 1c, we believe that steric compression forces a parallel mode of [2 + 2] cycloaddition. The symmetrically placed proximate O atom lone pair of electrons then has no effect and a 1:1 composition of the copolymer is observed. In other words the proximate O atom only has a major influence when there is substantial rotatory movement of the pπ orbitals of the C=C π-bond away from overlap in this moiety during the approach of the [Mt]=C and C=C partners in the [2 + 2] cycloaddition step.

3. Conclusion

The copolymerization of NBE and CPE in a variety of catalyst systems has been studied using ^{13}C NMR to analyse in detail the nature of the various dyads and triads formed. This has provided significant novel information about the sensitivity of the key [2 + 2] cycloaddition step in metathesis to steric and electronic factors associated with the [Mt]=C and C=C moieties involved.

Novel very high *cis* directing systems have also been developed for the homopolymerization of NBE using W, Mo, Os and Ru-based catalysts, and the general feature of *cis/trans* blockiness investigated in much greater detail. A clearer description of the associated relaxation processes of the propagation species emerges from this work. This is an important general aspect especially as the blockiness (tt pairs or t_n ($n > 2$) blocks in high cis polymers) in metathesis polymerization is exactly paralleled by the blockiness known as *error repair* and *error propagation* in Ziegler–Natta polymerization [17].

The metathesis copolymerization of the matched pair of monomers benzonorbornadiene and 7-oxa-benzonorbornadiene has also been

investigated using Os and Ru-based initiators and proven to be another valuable method of studying the electronic factors in the olefin metathesis mechanism. The subtle way whereby the presence of the proximate 7-O atom may facilitate [2 + 2] cycloadditions is highlighted here without the complication of a variable steric factor.

Acknowledgements

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