

Remarkable alternating effect in metathesis copolymerization of norbornene and cyclopentene using modified Grubbs ruthenium initiators

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Abstract

High *trans* and mainly *cis* directing Grubbs Ru initiators, I–III, and IV, respectively have been investigated as catalysts for metathesis copolymerization of norbornene and cyclopentene. When the Lewis acid, MoCl₅ or WCl₆, is added to these Lewis bases initiators, I–III, a cage effect develops such that the polymers become alternating caused by the severe or almost total denial of access of norbornene to the propagating metallocarbenes. Addition of ethers destroys the cages and removes the effect. In marked contrast the *N*-heterocyclic ligand Grubbs initiator, IV, does not show the effect, as addition of MoCl₅ only seems to retard the overall reaction, but does not change the copolymer composition.

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1. Introduction

Detailed ¹³C NMR spectra of copolymers of cycloalkenes reveal the microstructures of these materials, and at low conversions, constitutes a very valuable method of ascertaining the relative reactivities of the metallocarbenes involved. For example, extensive studies [1,2] have been carried out using norbornene (NBE = M₁) and cyclopentene (CPE = M₂) mixtures since NBE is more bulky than CPE, but its double bond is electronically much more reactive due to the great difference in strain energies of these cyclic substrates. The two metallocarbenes involved and the copolymer formed [2] are shown in Scheme 1 (P = polymer chain).

At low conversions and at different feed ratios one can obtain the overall competition ratio from M₂/M₁ ratios in the polymer. The intensities of the olefinic carbon atoms in the ¹³C NMR spectra afford the relative rate constants of the four kinetically distinct steps (Scheme 2).

Three *cis/trans* ratios (*c/t*), one for each of the homodyads M₂M₂ and M₁M₁, and one for the heterodyad $\frac{M_1M_2}{M_2M_1}$, may also be obtained, and then compared to those for the homopolymers alone using the same catalysts.

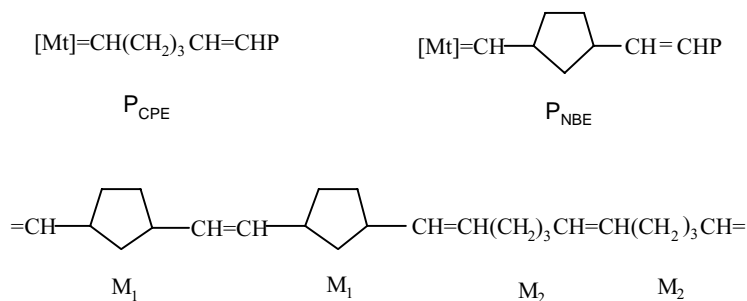
Each copolymer can be characterized by the value of the quotient, *r*, of the dyad concentrations:

$$r = \frac{[M_1M_1] \times [M_2M_2]}{[M_1M_2] \times [M_2M_1]}$$

where *r* = 1.0, the copolymer is random, while it is blocky for *r* ≫ 1.0, and alternating for *r* ≪ 0. If the ratio of monomer units in the polymer, *F* = [M₁]/[M₂], is expected to be high in favour of NBE, it is then appropriate to use a low molar feed ratio *f* = [M₁]/[M₂], in order to incorporate significant amounts of CPE. Under these conditions it is essential to analyse at very low conversions in order to obtain authentic (initial) values of *r*, and of the competition ratio, *F/f*. All these points are considered in the present work, where the less active noble metal catalysts are investigated, so that values of *F/f* will not be erroneously low and those of *r* too high, giving the copolymer a false appearance of blockiness.

The extremely active catalysts, e.g. MoCl₅/SnR₄ and WCl₆/SnR₄, used in chlorinated solvents, e.g. dichloromethane or chlorobenzene, yield random or slightly blocky copolymers [1] with competition ratios tending to one and *c/t* ratios also ~1.0. Such lack of selectivity both in *c/t* and competition ratios indicates that the [2 + 2] cycloaddition

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Scheme 1.

which is the key step in olefin metathesis is extremely rapid and is essentially diffusion controlled such that no discrimination, arising from the inherent steric and electronic differences of NBE and CPE, takes place. However, when ethers are used instead of solvents for these Mo and W-based catalysts, the Lewis base ether molecules tend to coordinate to the Lewis acid Mo and W cations involved thereby sterically crowding the [2 + 2] cycloaddition step such that the homopolymer of NBE becomes almost 100% *cis* [3,4]. Now the competition ratios are very high in favour of NBE, as almost no CPE is incorporated into the copolymer since this monomer is not electronically sufficiently active to enter into reaction with such sterically crowded metallacarbenes, especially P_{NBE} . On the other hand $RuCl_3 \cdot nH_2O$ as catalyst yields an essentially 100% *trans*-homopolymer of NBE and a copolymer where $F/f \sim 50$ in favour of NBE [2]. Again selectivity in *c/t* ratios are reflected in competition ratios as the metallacarbenes P_{NBE} and P_{CPE} with Ru ions are sufficiently less reactive as to render the [2 + 2] cycloaddition, steps (1) to (4) in Scheme 2, very sensitive to the steric and electronic natures of the monomers.

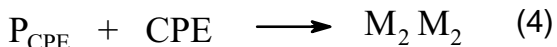
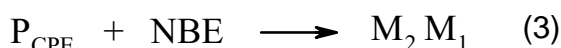
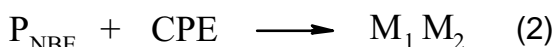
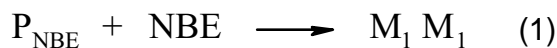
Remarkably when dry phenol is used as the solvent or in reagent quantities with the $RuCl_3 \cdot nH_2O$ catalyst, almost perfectly alternating copolymers of NBE and CPE ($r \sim 0.02$) are obtained [5,6]. This means that step (1) in forming M_1M_1 dyads is also disfavoured as well as step (4) for the M_2M_2 dyads, even though in the absence of phenol step (1) is by far that preferred. The *c/t* ratios are almost the same as those in the absence of phenol so the presence of the latter is not sterically crowding the [2 + 2] cycloaddition steps.

We originally believed that the active site was a Ru[phenoxide] species [5]. However, microanalyses of

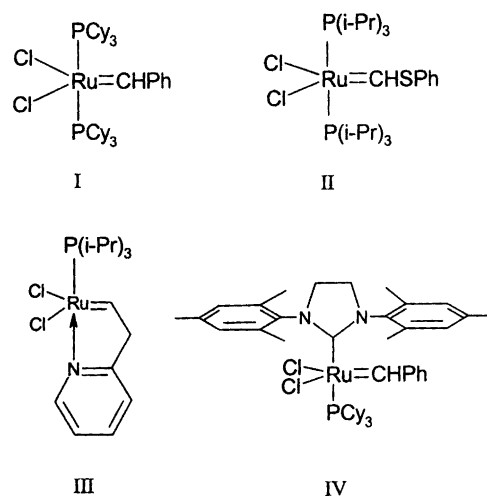
samples of $RuCl_3$ subjected to several cycles of heating in dry phenol followed by removal of this solvent under high vacuum revealed the same amount of chlorine as in the original sample (42.9% versus 42.3% after treatment) [6]. This evidence, and the fact that halogen ions bonded to metal can act as hydrogen-bonding acceptors [7,8], led us to postulate a catalyst site based on $RuCl_3$ with phenol molecules hydrogen-bonded to the chloride ions [5]. A cage is formed around the Ru ion such that the more bulky NBE is largely denied access to the reaction centre when the more bulky metallacarbene P_{NBE} is the propagating species. The very low content of the homodyads, M_2M_2 , in the copolymer is then due to the very discriminating nature of P_{CPE} , in favour of step (3) in competition with step (4) in Scheme 2.

Using $OsCl_3 \cdot nH_2O$ as catalyst, this cage effect is so severe that NBE is denied access by both P_{NBE} and P_{CPE} such that only a homopolymer of CPE is formed from NBE/CPE mixtures [5]. When small amounts of water are also added to these Ru and Os-based catalyst systems the cage effect is eliminated and the copolymers are then similar to those normally observed in the absence of phenol [6].

In the light of all of this it was therefore useful to study the behaviour of the well-defined Ru initiators, I–IV, in various solvents and reagents for the copolymerization reactions of NBE and CPE.



Scheme 2.



2. Experimental

All the initiators were first tested using a 4/1 molar feed ratio of CPE/NBE in a suitable dry solvent mainly dichloromethane, and quenching the reaction as already described in [2] in order to keep the yield <10%. Both the reagents and the solvents were dried by distillation before use. In a typical experiment 0.15 g NBE, 0.43 g CPE and 4 mg of initiator were mixed at room temperature in 3 ml of dry solvent. Ethyl vinyl ether was used routinely to quench the reaction at low yield. ^{13}C NMR spectra of the polymers in CDCl_3 were recorded on a Bruker Avance DPX 500 spectrometer at 125 MHz.

3. Results and discussion

The behaviour of catalysts I–III was essentially the same. The olefinic region of the ^{13}C NMR spectrum of the copolymer made using I is shown in Fig. 1.

The competition ratios are ~ 8 in favour of NBE and the *cis* contents are low, $\sim 15\%$, for M_1M_1 , as for the homopolymer. The main novel point of interest is that the blockiness parameter, $r = 0.37$, shows that the copolymer has some tendency to alternate. This is attributed to an intrinsically low activity of P_{CPE} such that it is relatively more discriminating towards NBE than CPE when compared to P_{NBE} , even

though the latter has adverse increased steric bulk [ratio of rates: step (3)/step (4) > step (1)/step (2)]. P_{CPE} is believed to relax more readily to an electronically more stable geometry between propagating steps than the more bulky and more rigid P_{NBE} [3].

When the reaction is carried out in dry dioxan, the results using I–III are essentially the same as those obtained using dichloromethane as solvent. By way of contrast when the more Lewis acid catalysts, MoCl_5 and WCl_6 , with SnR_4 as cocatalyst, are used in ethers, the *cis* content of M_1M_1 in the copolymer is $\sim 100\%$ and there is almost no incorporation of CPE [2]. This difference suggested that it would be of interest to study the effect of Lewis acids on these basic Grubbs initiators [9] by adding MoCl_5 or WCl_6 at 10–20-fold molar excess with respect to initiators I–III both in dichloromethane and dioxan as solvent.

Using MoCl_5 first in dichloromethane the results are as shown in Fig. 2. Now a strongly alternating copolymer is formed ($r = 0.01\text{--}0.02$) just as previously observed using the $\text{RuCl}_3 \cdot n\text{H}_2\text{O}/\text{phenol}$ catalyst system [5,6], but the *cis* content of M_1M_1 dyads remains the same. We believe that the MoCl_5 is engaging I–III and forming a cage around the metallacarbene by virtue of extended Lewis acid–Lewis base bonding, such that access of NBE to P_{NBE} is largely prevented; an analogous hydrogen-bonded cage in the $\text{RuCl}_3 \cdot n\text{H}_2\text{O}/\text{phenol}$ catalyst system seems to form and have the same effect. The normally predominant step

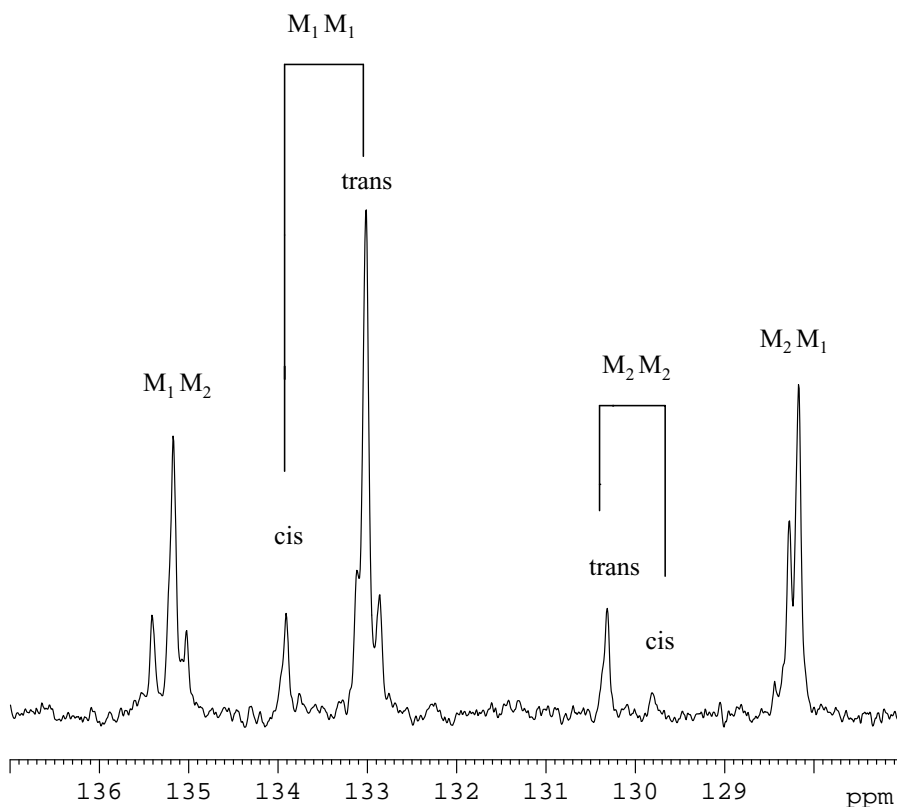


Fig. 1. Copolymer using Grubbs initiator I in dichloromethane.

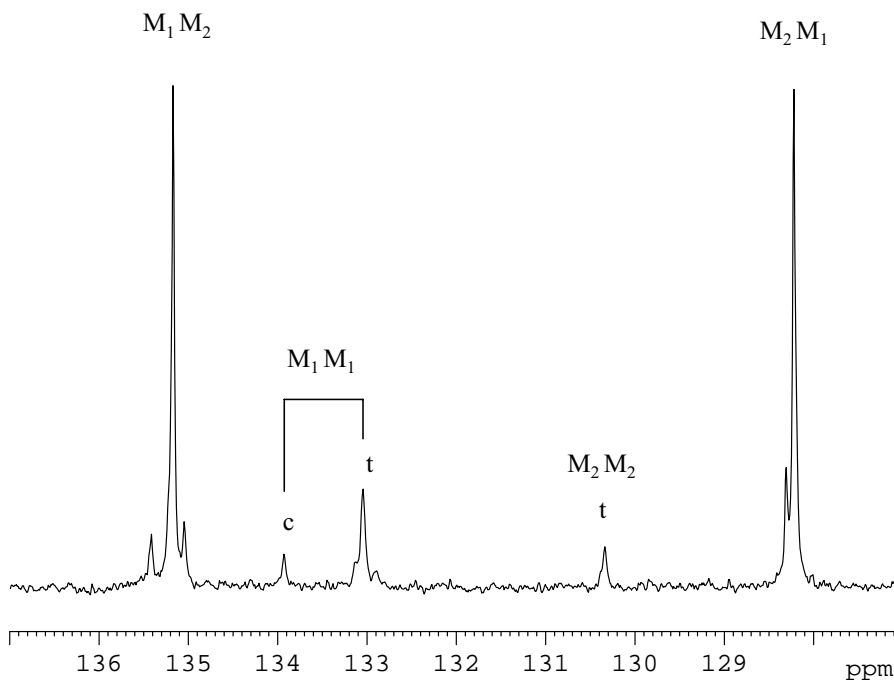


Fig. 2. Copolymer using Grubbs initiator I with MoCl_5 in dichloromethane.

(1) is almost entirely excluded because P_{NBE} and NBE are respectively sterically more bulky than their counterparts.

When the experiments are carried out in dry dioxan as solvent the results are as shown in Fig. 3. Clearly Lewis base ethers disrupt the cage so that the sieving effect is eliminated

as the $[\text{Ru}]-\text{Cl} \cdots \text{MoCl}_5 \cdots \text{MoCl}_5$ dative bonds are then broken. The *cis* content of the M_1M_1 units always remains the same showing that potential $[\text{Mo}]$ -carbenes are not the source of metathesis but the $[\text{Ru}]$ initiators are. MoCl_5 had the same effect on II as on I and III in dichloromethane

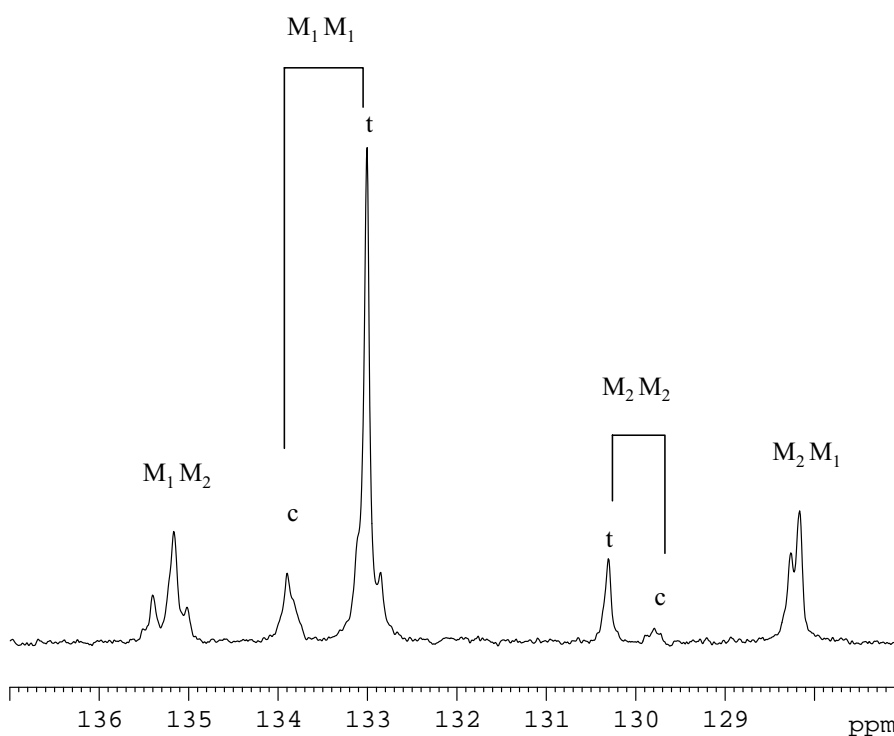


Fig. 3. Copolymer using Grubbs initiator I with MoCl_5 in dioxan.

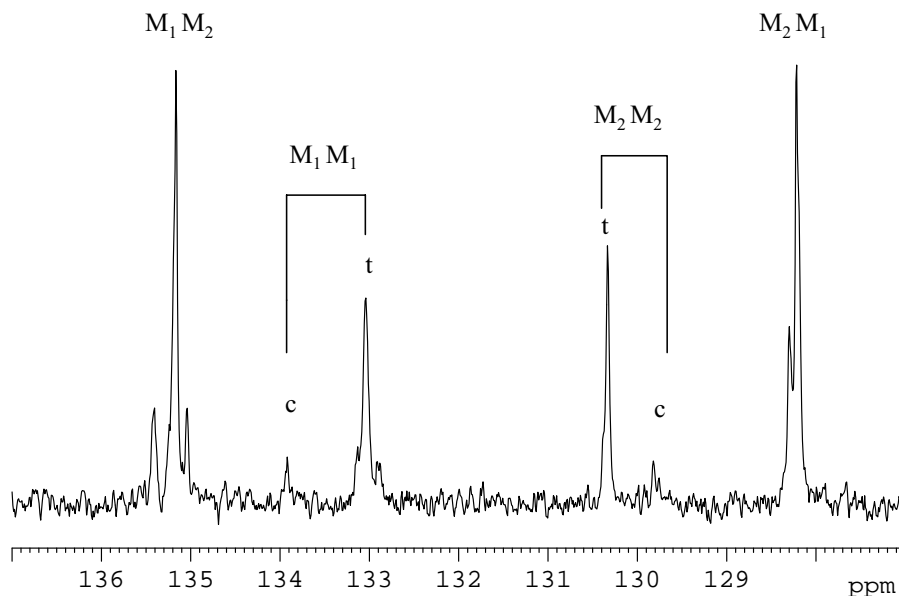


Fig. 4. Copolymer using Grubbs initiator II with MoCl_5 in dichloromethane.

but to a lesser extent ($r = 0.25$) (Fig. 4). This change is attributed to the fact that II contains a thioether group that may compete with Cl^- ligands in dative bonding to MoCl_5 thereby reducing somewhat the cage effect.

Replacing MoCl_5 by WCl_6 in these experiments has the dramatic effect of almost eliminating steps (2) and (3) as well as step (1) (Fig. 5) just as found for the $\text{OsCl}_3 \cdot n\text{H}_2\text{O}$ /phenol catalyst system [5]. Obviously the caging effect on P_{NBE}

is now more severe such that P_{CPE} is largely responsible for reaction forming mainly M_2M_2 dyads, i.e. almost a homopolymer. Again using ether as solvent the copolymer is normal, similar to that shown in Fig. 1, so the WCl_6 effect is cancelled by the Lewis base. The large excess of both MoCl_5 and WCl_6 seems to be necessary to produce these dramatic effects since in experiments where the amounts of both these metal salts in dichloromethane were reduced by

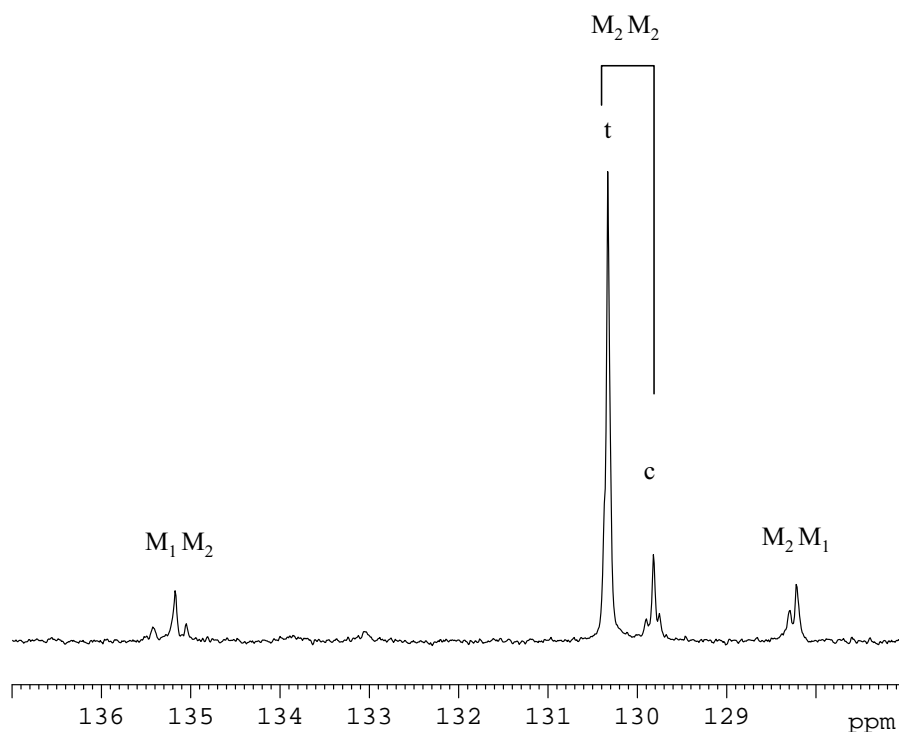


Fig. 5. Copolymer using Grubbs initiator I with WCl_6 in dichloromethane.

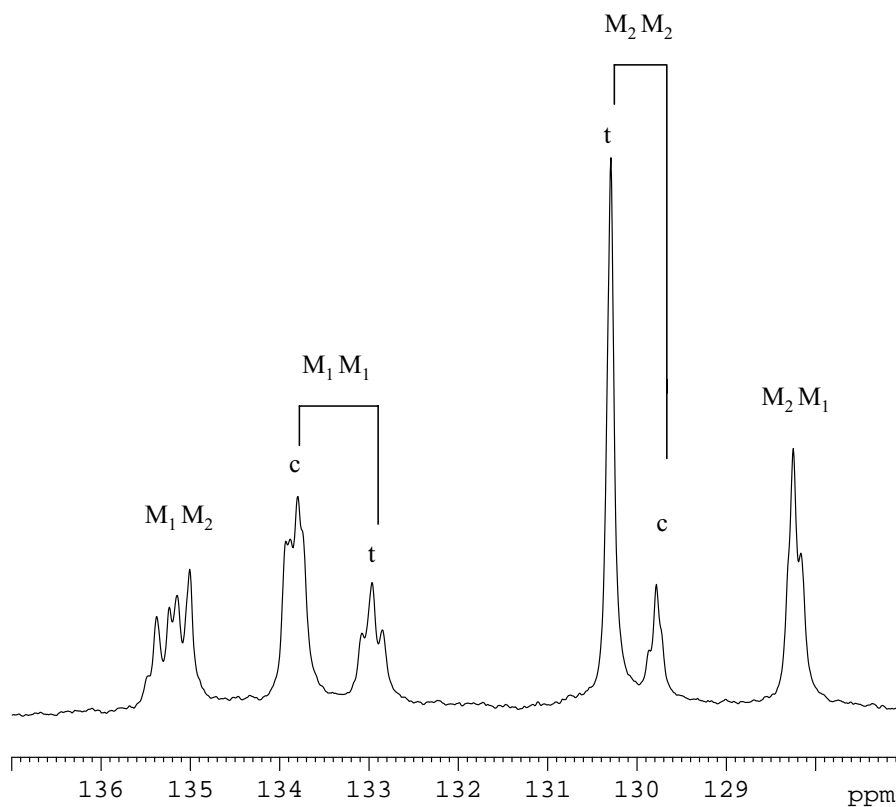
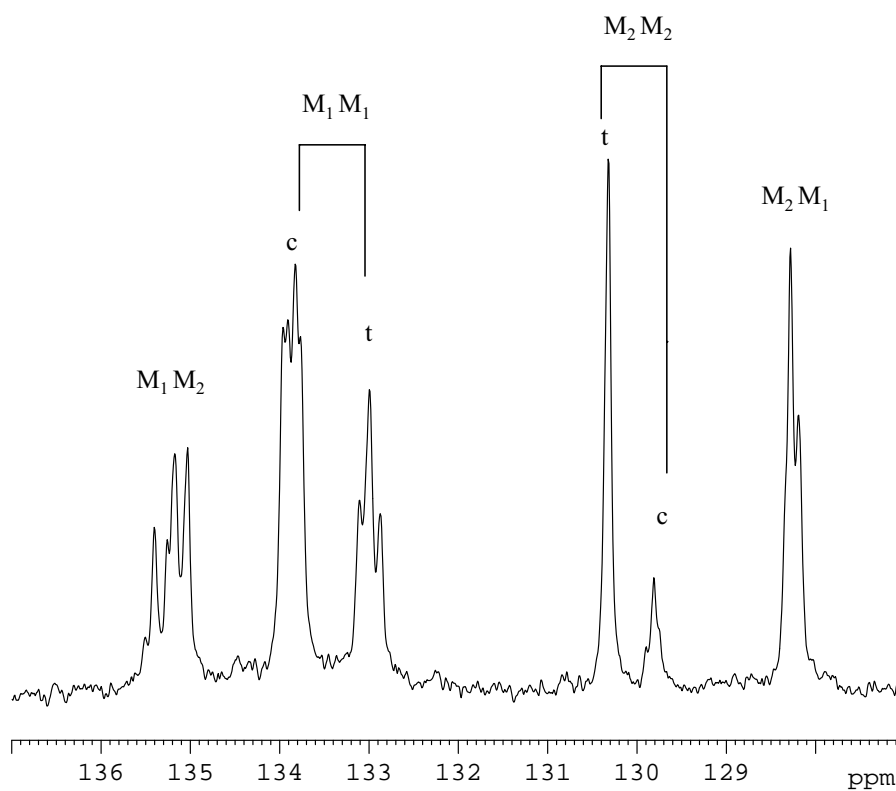


Fig. 6. Copolymer using Grubbs initiator IV in dichloromethane.

Fig. 7. Copolymer using Grubbs initiator IV with MoCl_5 in dichloromethane.

a factor of five, the polymers showed only a slight trend in the direction of alternation, and their ^{13}C NMR spectra resembled that shown in Fig. 1.

By way of contrast, catalyst IV in dichloromethane forms a product whose ^{13}C NMR spectrum (Fig. 6) shows that now there is a much greater incorporation of CPE into the copolymer which tends to be somewhat blocky ($r \sim 2.0$) rather than alternating. The M_1M_1 units are now more *cis* ($\sigma_c = 57\%$) whereas the M_2M_2 units remain highly *trans* ($\sigma_t = 81\%$) in contrast to the behaviour observed using I–III where all dyads are mainly *trans*.

When MoCl_5 is added to IV, copolymer is formed extremely slowly (80 h for 4% yield compared to 40 min in the absence of the MoCl_5). However, the ^{13}C NMR spectrum of the product (Fig. 7) is similar to that in Fig. 6 with $r = 1.9$. This shows that, in contrast to its behaviour with I–III, MoCl_5 is acting here as a reversible poison for all the propagating steps such that only a very low concentration of MoCl_5 -free metallacarbenes are present at any instant and then propagate the normal reaction.

The *cis* content of M_2M_2 dyads which is almost the same as that for homopolymer of NBE using IV ($\sigma_c = 61\%$), shows that the steric factor is very important here presumably because of the bulk of the *N*-heterocyclic ligand. The steric factor exerts a dominant effect on the relative rates of steps (3) and (4) such that the rate ratio inequality producing blockiness is: step (1)/step (2) > step (3)/step (4), in contrast to the inequality, step (1)/step (2) < step (3)/step (4), for catalysts I–III, which causes the alternating tendency.

The effect of dry *p*-chlorophenol, as well as phenol, instead of dichloromethane, as solvent on the copolymerization using Grubbs initiator I was also checked. However, while this resulted in an increase of the overall activity, the strongly alternating behaviour found using *p*-chlorophenol with $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ [5,6], was not observed; the microstructures showed a three-fold increase in the normally very low concentrations of M_2M_2 dyads (Fig. 1), and an increase of the *cis* content of M_1M_1 from 15 to 28%.

4. Conclusion

The caging effects on copolymerization found previously using $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ with phenol and then $\text{OsCl}_3 \cdot n\text{H}_2\text{O}$ with phenol [5,6] are exactly matched using Grubbs initiators I–III with MoCl_5 , and then with WCl_6 , respectively, but are not observed using the more *cis* directing catalyst, IV, where the presence of MoCl_5 merely acts as a strong reversible poison for all propagating steps. The effect is attributed to

hydrogen bonding in the metal salt/phenol systems, and, in accordance with that idea, is reversed by adding a little water which disrupts the cage walls. On the other hand the cages with Grubbs initiators seem to form via: Lewis acid–Lewis base bonding, e.g. $[\text{Ru}]-\text{Cl} \cdots \text{MoCl}_5 \cdots$, and are disrupted by addition of ethers. There is recent evidence that Grubbs initiators act as Lewis bases [9].

This effect is novel and remarkable in the metathesis polymerization field since the cages apparently control access of the monomers to the metallacarbene, but do not sterically compress the [2 + 2] cycloaddition step, as the *cis* contents of the dyads are not affected. The effect is also dynamic as the cage walls are apparently disrupted by addition of competitive hydrogen-bonding and Lewis base agents, respectively. It is worth noting that the influences of such cage effects on stereoselectivities are well-known in catalysis involving zeolites [10] and cyclodextrins [11], but the present example is highly novel and remarkable for polymer chemistry.

Acknowledgements

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