The remarkable activity of 7-oxa-benzonorbornadiene in metathesis copolymerization using Ru-based initiators

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Abstract

The comparative reactivity of 7-oxa-benzonorbornadiene in metathesis copolymerization reactions using Ru-based initiators has been investigated. It is as reactive as norbornene, about 8 times more reactive than cyclopentene, and at least 19 times more reactive than benzonorbornadiene. The role of the proximate 7-oxygen atom in facilitating the transition state of the $[2 + 2]$ cycloaddition step is discussed.
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1. Introduction

When an ether oxygen atom is present in norbornenes and norbornadienes and is very proximate to the double bond participating in the $[2+2]$ cycloaddition step which is central to olefin metathesis, it can greatly enhance the reactivity of these cycloalkenes and cycloalkadienes. Thus, the ROMP of 7-*t*-butoxynorbornadiene shows the surprising result for several catalyst systems, especially those which are Mo-based, that there is little *syn/anti* discrimination in the orientation of monomer insertion into the growing polymer chain [1–3] even though the *syn-exo* face orientation is strongly disfavoured on steric grounds as confirmed by the observation that there is a strong bias in favour of the *anti* orientation in the ROMP of 7-methylnorbornadiene [4] using the same catalysts. A lone pair of electrons on the O atom that is proximate to the *syn* double bond in 7-*t*-butoxynorbornadiene must therefore mix in with the two key pairs of electrons involved in $[2 + 2]$ cycloaddition step thereby facilitating the *syn* orientation. The observation that in the $[2 + 2]$ cycloaddition of benzyne to 7-*t*-butoxynorbornadiene the *syn-exo* face is also preferred to the *anti* orientation [5] confirms this idea, since transition metal ions that potentially complicate any theoretical explanation are absent here.

A very good way of studying the comparative reactivities of substrate olefins and metallacarbenes in metathesis is to analyse the microstructures of copolymers at low conversions using detailed ^{13}C NMR spectra. We have applied this approach very extensively using norbornene (NBE) and cyclopentene (CPE) [3,6,7] and especially for well-defined Ru-based Grubbs initiators [8] under a variety of conditions. In this pair of monomers, NBE is more bulky than CPE, but this adverse steric factor is offset by the fact that the former is highly strained so its double bond is electronically much more reactive. Furthermore, the lines in the ^{13}C NMR spectra for all the olefinic C atoms are very clearly resolved such that compositional blockiness, and c/t ratios for homodyads, M_1M_1, are all readily determined [3].

The copolymer methodology can also be extended to studies of the proximate O atom effect. Here matched pairs are used where the only change from one partner to the other in the monomers is the replacement of the 7-CH_2, at the bridge position, by an O atom, in both norbornenes and norbornadienes [2]. A particularly useful example of such a pair is 7-oxa-benzonorbornadiene (OBNBD) and benzonorbornadiene (BNBD) where a strong bias in favour of insertion of OBNBD into the growing polymer chain has been noted using $RuCl_3 \cdot nH_2O$ as catalyst [2]. Schrock and co-workers [9] had also observed using well-defined Mo-carbene initiators that various 7-oxa-norbornenes and 7-oxa-norbornadienes undergo metallacyclobutanation more readily than their CH_2 bridged analogues and attributed this to chelation through the 7-oxygen atom. However, while this may be true using Mo-based systems, as shown by the effect of the ether solvents in greatly increasing c/t ratios in

=CH⎤   ⎡CH= is a NBE, CPE, or a BNBD unit.
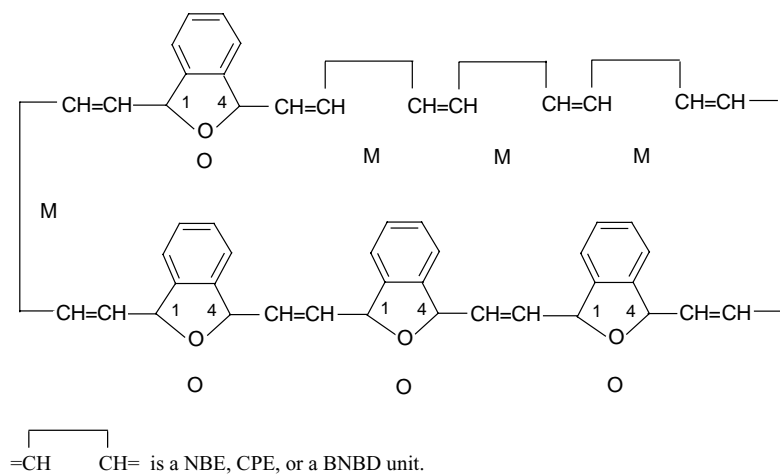
Scheme 1.
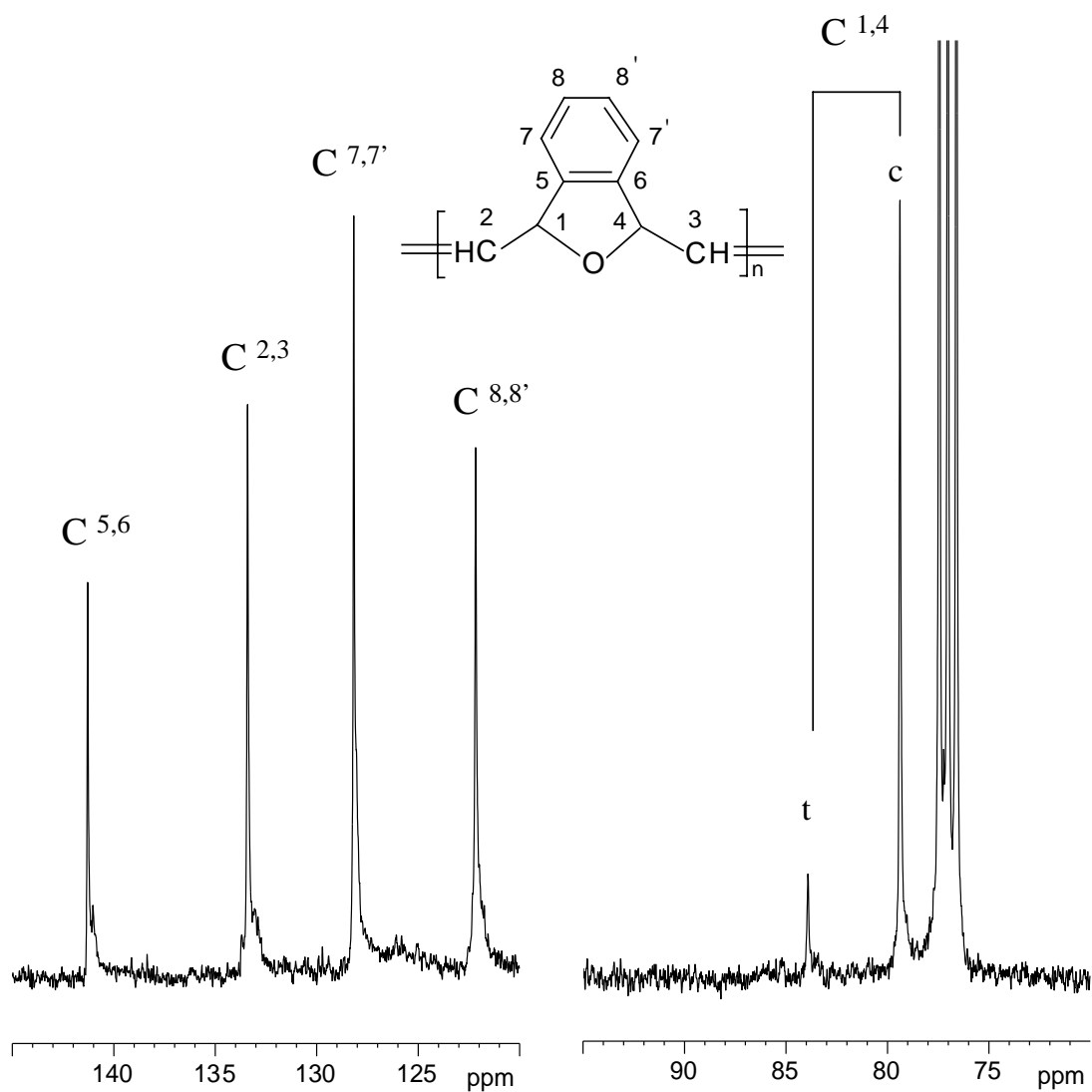
Fig. 1. Poly-OBNBD made using MoCl$_5$/SnMe$_4$ catalyst.

poly-NBE made using Mo-based catalysts [7], it is a much less likely explanation for Ru-based catalysts where ethers have no such effect [7]. In the present work, we therefore decided to examine the comparative reactivity of OBNBD with BNBD, NBE, and CPE, using the Grubbs initiators $(PCy_3)_2Cl_2 Ru=CHPh$ (I) and $IMesH_2(PCy_3)Cl_2Ru=CHPh$ ($IMesH_2$ = 1,3-dimesithyl-4,5-dihydroimidazol-2-ylidene) (II). The OBNBD monomer is particularly interesting in view of our previous results [2] using $RuCl_3 \cdot nH_2O$, and the very brief report [10] that, with a $Ru(H_2O)_6(tos)_2$ catalyst, it is found to be explosively reactive.

Previous work [2] had shown that the compositions of the copolymers of OBNBD and BNBD are easily estimated from the ^{13}C NMR line intensities for the respective C^1 and C^4 carbon atoms, but that there was great overlap of the resonances for the olefinic carbon atoms. Comparisons with ^{13}C NMR spectra of poly-NBE and poly-CPE [3] showed that overlap of the ^{13}C NMR lines for the olefinic C atoms

would also be major here, but that clear resolution of the resonances for the respective C^1 and C^4 atoms should still be possible. The composition of all possible copolymers and triad units for the three pairs, OBNBD and BNBD, OBNBD and NBE, OBNBD and CPE, are shown in Scheme 1, where the C^1 and C^4 atoms of special interest are highlighted.

The four triads, with an O unit at the centre, of interest for the different C^1 and C^4 resonances, are MM, $\underline{M}$O, M$\underline{O}$, and OO.

2. Experimental

The diene monomers were prepared and purified according to procedures previously described in the literature for OBNBD [11] and BNBD [12]. NBE, CPE and dichloromethane were distilled from CaH_2 and chlorobenzene was distilled from P_2O_5 before use. The Grubbs
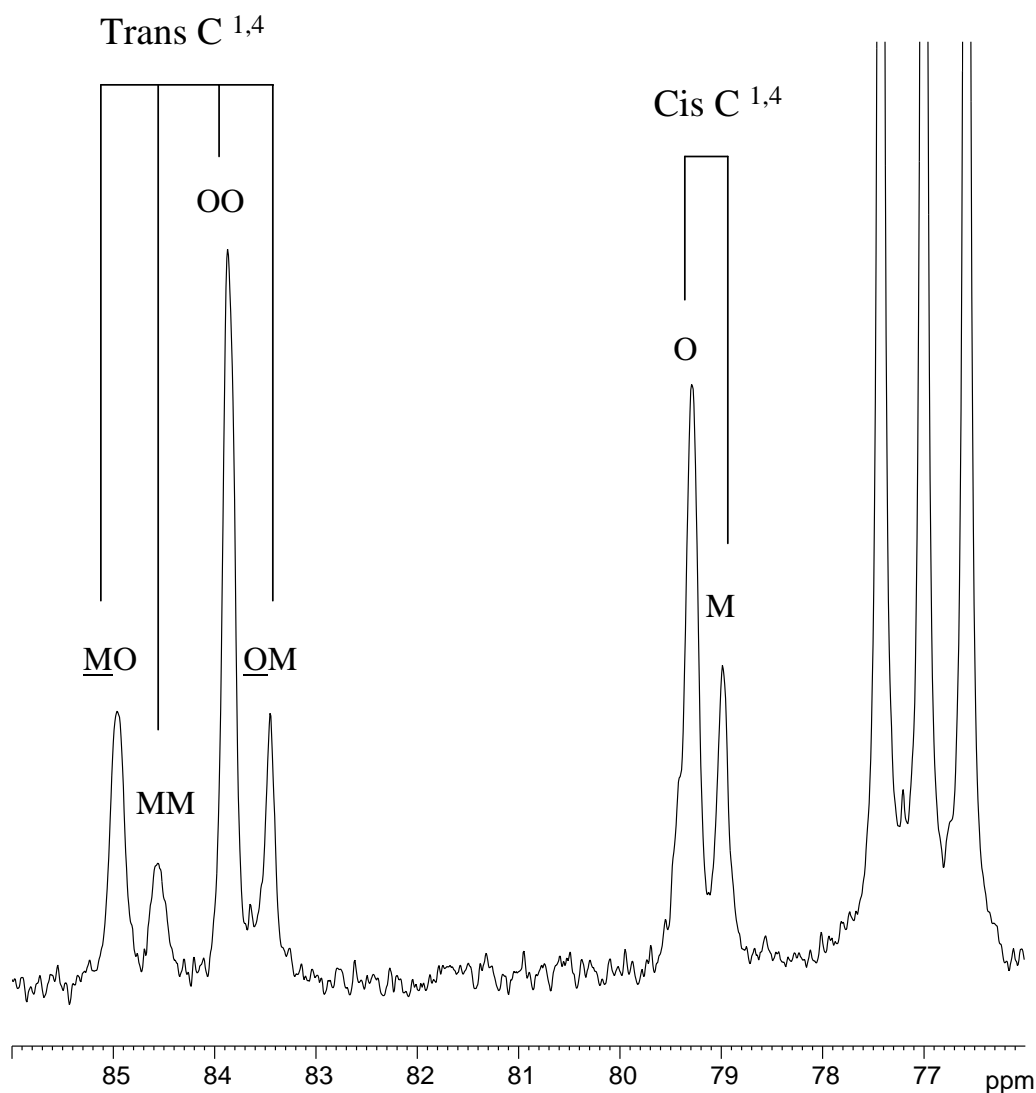

Fig. 2. Copolymer made from OBNBD and NBE using Grubbs initiator I and 2/1 monomer feed ratio.

initiators I and II (5 mg) were tested in dry dichloromethane at different molar ratios of monomers. $MoCl_5$ (30 mg)/$SnMe_4$ catalyst system was tested in dry chlorobenzene. Typically, a 100 mg sample of OBNBD was used and the mixture of the two monomers in solution in appropriate solvent (2.0 ml) was added to the catalyst solution (1.0 ml). The reaction was quenched within minutes with ethyl vinyl ether [8] in order to keep the conversion of OBNBD ≤10%. ^{13}C NMR spectra of the copolymers in $CDCl_3$ were recorded on a Bruker Avance DPX 500 spectrometer at 125 MHz.

3. Results and discussion

Since OBNBD is an ether, and the presence of ethers through coordination to the Lewis-acid metal ions drives up the *cis* content of poly-NBE with MoCl$_5$-based catalysts [7], we first made homopolymer of OBNBD using a $MoCl_5$/$SnMe_4$ catalyst. As expected the fraction of *cis* double bond is high, $\sigma_c = 0.86$, whereas $\sigma_c = 0.67$ for poly-BNBD made with this catalyst. The ^{13}C NMR spectrum of poly-OBNBD is shown in Fig. 1.

It is remarkable that there is no *m/r* or *c/t* splitting in all the lines, and this was confirmed when poly-OBNBD was made using initiator I, where $\sigma_c = 0.46$. Here, as expected, the presence of the ether groups had no effect on the σ_c value, and this was confirmed since the same value of $\sigma_c = 0.46$ was estimated for poly-BNBD, also made using I.

Copolymers using Grubbs initiators I and II were then prepared and analysed. A 2/1 molar feed ratio of OBNBD and NBE was first investigated with I and the spectrum is shown in Fig. 2.

The C^1 and C^4 resonances of the O units were now resolved by flanking O and M units into an MM, MO, OM, and OO quartet for $C^{1,4}$ *trans*, and as a doublet for $C^{1,4}$ *cis*. The *cis* content, σ'_c, of the OM and OO dyads was
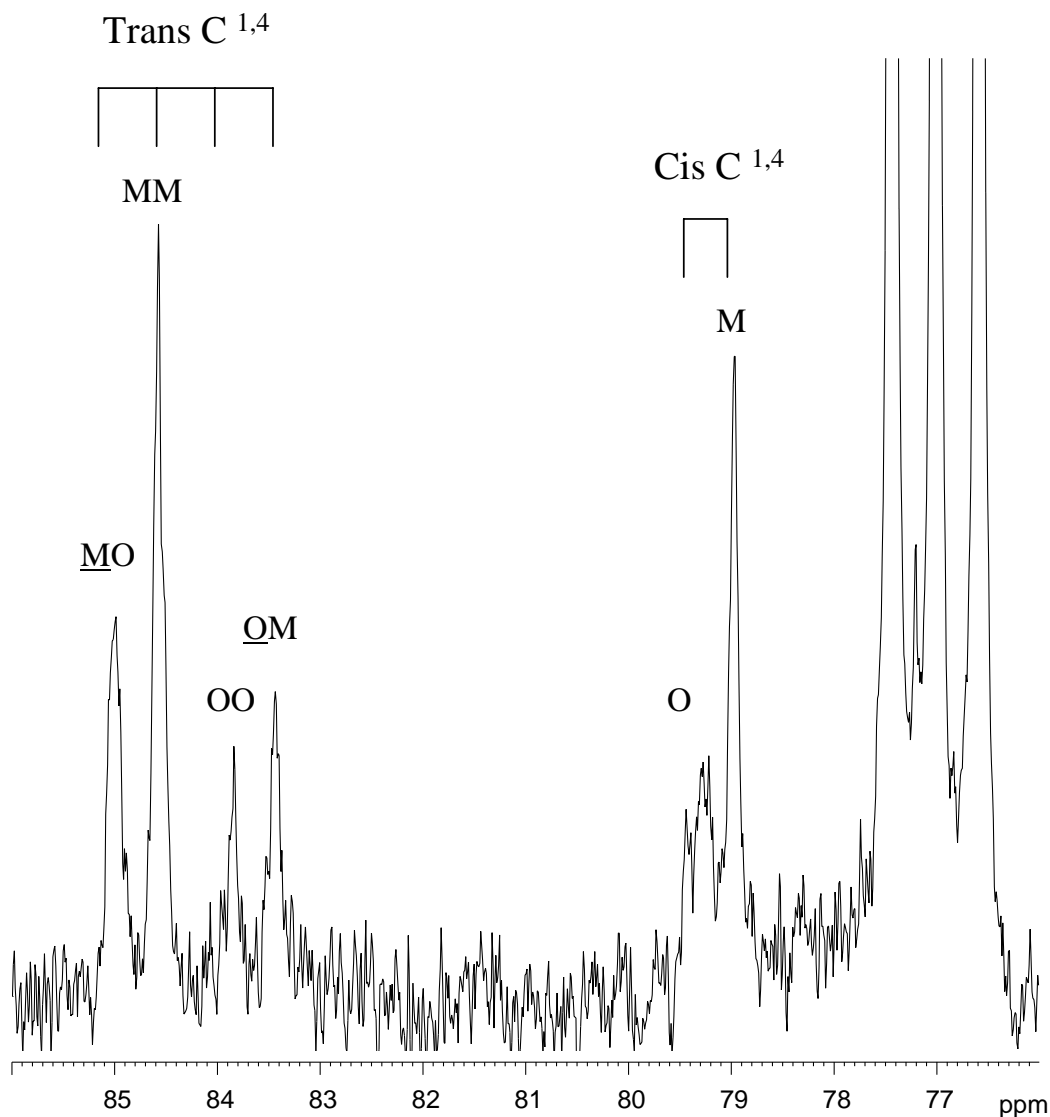

Fig. 3. Copolymer made from OBNBD and NBE using Grubbs initiator I and 1/2 monomer feed ratio.

estimated as $\sigma_c = 0.41$. The quartet and doublet show, respectively, that the copolymer is essentially random, $r = MM \times OO/QM \times O\underline{M} = 1.4$ and the competition ratio is ~ 1.0. The weaker lines for $C^{1,4}$, $C^{5,6}$, and C^7 resonances of the MM dyads showed considerable overlap and complexity arising from further O/M and *c/t* splitting, and were not considered.

In order to confirm the analysis of Fig. 2, a 1/2 molar feed ratio of OBNBD and NBE was then used with I, and the spectrum of the copolymer obtained is shown in Fig. 3. The relative intensities of the lines in the $C^{1,4}$ *trans* quartet is as expected and $\sigma_c' = 0.30$. In this case, the C^7 triplets for the MMM triads was much stronger and cleaner, so we were able to estimate for these units, $\sigma_c = 0.43$, and blockiness, $r_t \times r_c = (tt \times cc)/(ct \times tc) = 6.5 \times 5 = 32.5$. Since poly-NBE made using initiator I has $\sigma_c = 0.15$ and is random [8], the presence of OBNBD is increasing the *cis* content of the MMM triads and is making these extremely blocky (32.5). The probable explanation is that OBNBD is acting "on and off" as a spectator ligand of the Ru ion while a string of M

units is added into the copolymer. When OBNBD is off, I is high *trans* directing in making poly-NBE, as is normal [8], but when it is on, I becomes sterically crowded and the direction is high *cis*.

Initiator II afforded a copolymer using a 2/1 molar feed ratio of OBNBD and NBE whose spectrum is shown in Fig. 4, which is very similar to that in Fig. 2. The only difference as expected, since II is more *cis* directing than I [8], is that the $\sigma_c' = 0.66$. The higher σ_c' value is in accordance with the fact that $\sigma_c = 0.64$ for poly-NBE made using II where the bulky N-heterocyclic ligand sterically crowds propagation.

A copolymer using a 1/4 molar feed ratio of OBNBD and CPE was next prepared and its ^{13}C spectrum is shown in Fig. 5. Again a random polymer is detected but since the O/M content is $\sim 2/1$, the competition ratio is ~ 8.0. This is also the ratio found when NBE and CPE are copolymerized using I [8], and further confirms that OBNBD is very reactive, comparable to NBE itself. The *cis* content from Fig. 5, $\sigma_c' = 0.57$. It is worth noting that since I is very highly *trans* directing for both NBE and CPE, while II is only high trans
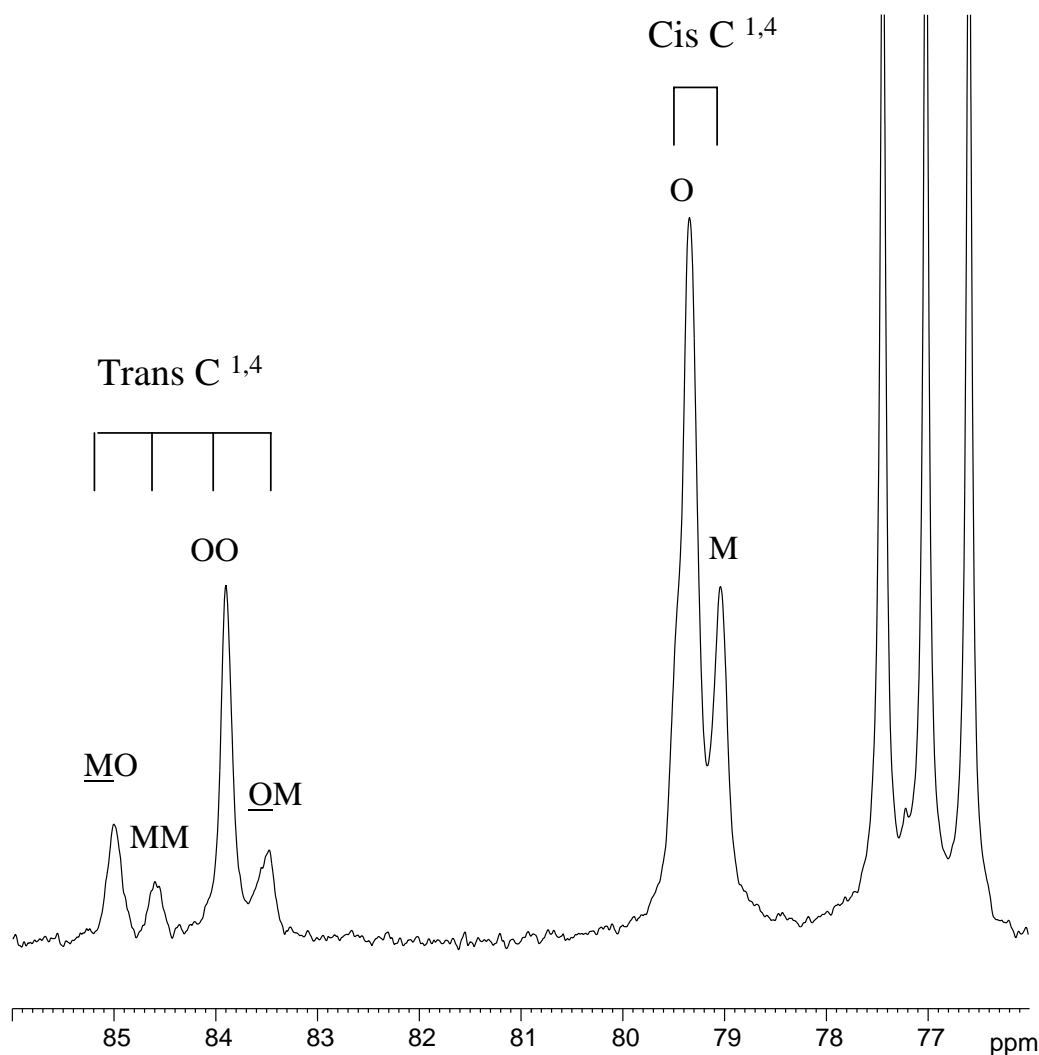

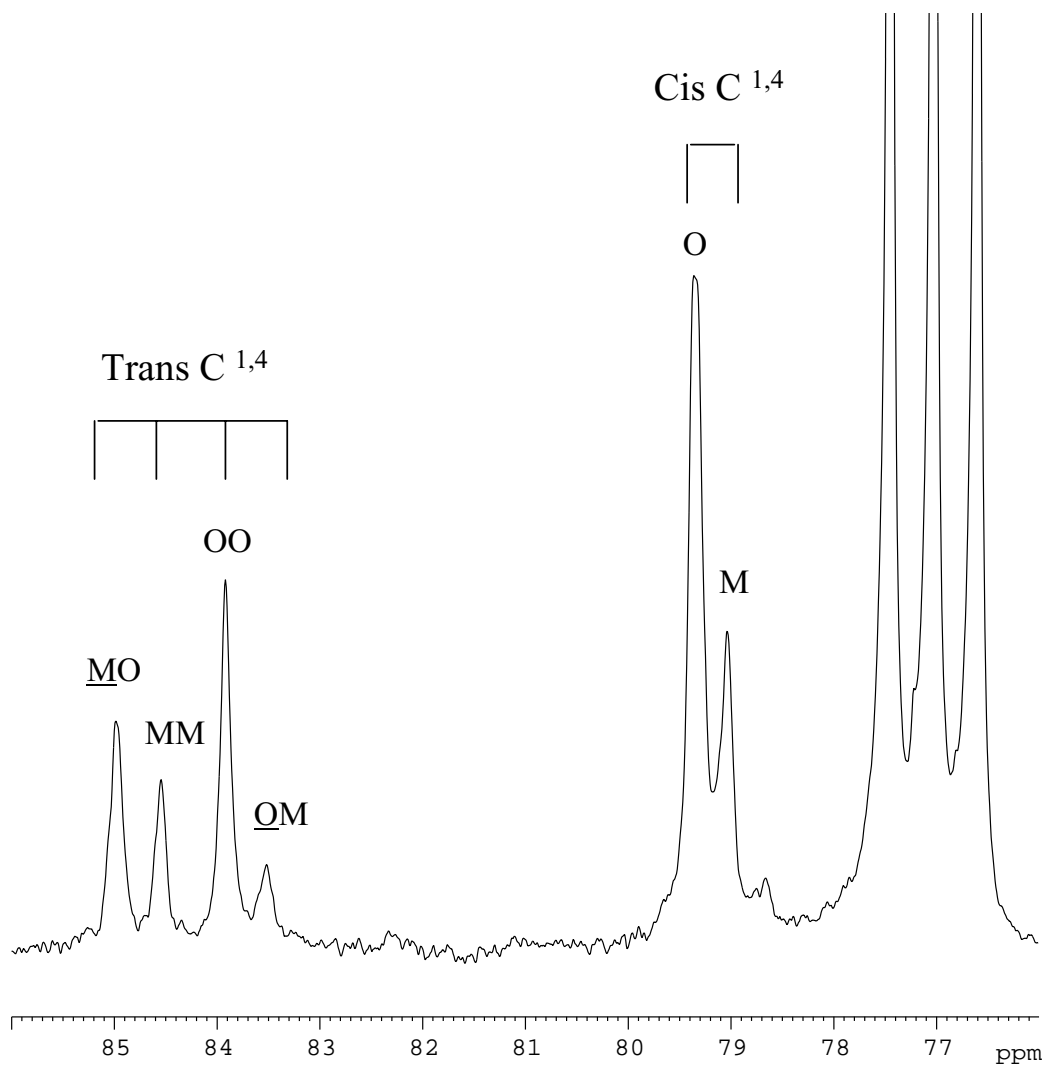Fig. 4. Copolymer of OBNBD and NBE made using Grubbs initiator II and 2/1 monomer feed ratio.

Fig. 5. Copolymer of OBNBD and CPE made using Grubbs initiator II and 1/4 monomer feed ratio.

directing for CPE, σ'_c values which are estimated for both OM and OO dyads, together, are expected to be intermediate in size, as obtained. However, since σ_c for poly-NBE is also high, as well as σ_c for poly-OBNBD made using II, σ'_c is also as large.

Finally a 1/1 molar feed ratio of OBNBD and BNBD was used with I. There was very little incorporation of the latter since the O monomer content of the copolymer was estimated as ≥95%. When a check was carried out using $RuCl_3 \cdot nH_2O$ as catalyst, the same result was obtained but $\sigma'_c = 0.25$ compared to $\sigma'_c = 0.46$, using I. Since OBNBD and BNBD are matched in size this is a striking illustration of the beneficial effect of the presence of 7-oxygen atom on reactivity.

All the results confirm the above conclusion with Ru-based catalysts, and in contrast to Mo-based catalysts there is no evidence that this arises from chelation via the *exo* face of the double bond and the proximate O atom. Rather, the O atom *syn* lone pair of electrons is apparently mixing in and weakening the p^{Π}–p^{Π} overlap of the double bond

in OBNBD, thereby facilitating the [2 + 2] cyclobutanation step. This is very important for Ru-based catalysts where the metallacarbenes are more basic [13] and less reactive than those that are Mo-based; the interaction of the electron pairs can be depicted in valence bond language in Scheme 2.

Conjugation through the O atom to the benzo group may be important as shown, but the effect of the O atom in 7-*t*-butoxynorbornadiene [2 + 2] cycloadditions [5] shows that is not essential.
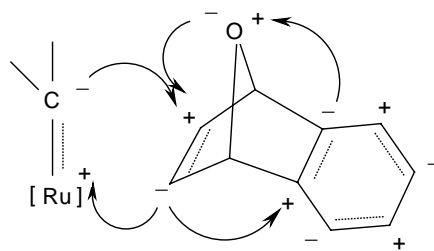
Scheme 2.

4. Conclusion

Generally [2 + 2] cycloaddition reactions of alkenes are thermally disfavoured on theoretical grounds (Woodward–Hoffmann rules), while [4 + 2] cycloadditions, Diels–Alder reactions, are allowed. The present work shows that mixing in a third pair of electrons in the [2 + 2] cyclobutanation transition state also facilitates metathesis using Ru-based initiators. However, all these copolymerization reactions could be investigated further using the well-defined Schrock Mo-based initiators [9], where chelation may well be an important factor.

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