

Ring-opening Metathesis Polymerization of 7-*tert*-Butoxybicyclo[2.2.1]hepta-2,5-diene

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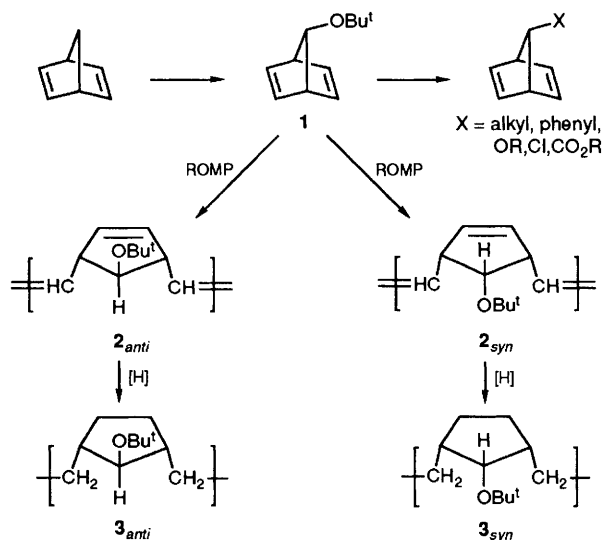
Novel ring-opened metathesis polymers are prepared from 7-*tert*-butoxybicyclo[2.2.1]hepta-2,5-diene and various 7-substituted derivatives using two initiators; their microstructures provide evidence that propagation occurs through the *endo* as well as the *exo* faces.

Ring-opening metathesis polymerization (ROMP) of 7-alkyl-norbornenes¹ shows that reactivities of the 7-*syn* isomer are strongly retarded whereas the 7-*anti* isomers are almost as reactive as norbornene (NBE) itself. The following explanation has been suggested. Inhibition of attack, by a propagating metallacarbene on the *endo* face of NBE and all its derivatives is expected, but in the specific case of the 7-*syn* isomer the *exo* face is also sterically very hindered.

Norbornadiene (NBD) is often less readily polymerized than NBE especially when noble metal catalyst systems are used;² the high *cis* content of the polymers in some cases and the lack of reactivity in others indicates a tendency to have one monomer molecule present as a di-*endo* bidentate spectator ligand on the metal complex thereby totally inhibiting the metathesis reaction or sterically inducing the less bulky *cis* orientation in metallacycle formation with the incoming monomer.³ Since 7-*tert*-butoxybicyclo[2.2.1]hepta-2,5-diene, **1**,

may be prepared from NBD using readily available reagents⁴ and may in turn be converted into a whole range of 7-substituted derivatives^{4,5} we decided to make these compounds and to examine them as monomers for the synthesis of novel ROMP polymers such as soluble poly(norbornadienes), which may then be converted into soluble conjugated polyenes by dehydrogenation.⁶ Here, we report that this new class of monomer has made possible the investigation of the orientation of attack in the propagation step in which two of the four possible modes may be distinguished, (*endo-syn/exo-syn*) and (*endo-anti/exo-anti*).

Many catalytic systems were tried but so far only two initiators, Et₂O-modified MoCl₅/SnMe₄[†] and OsCl₃[‡] have been found to be active. High molecular mass polymers are also obtained using the 7-methoxy and 7-acetoxy analogues of **1**: the detailed analysis of these materials will be reported elsewhere. The ¹³C NMR spectra§ of the polymers obtained from **1** are shown in Fig. 1 and assigned to the structure **2** on the basis of the various line positions and intensities.



Scheme 1

[†] The MoCl₅ reactions were carried out in serum-capped flasks at ambient temperatures. Thus a 0.18 mol dm⁻³ solution of MoCl₅ in dry chlorobenzene was treated with an equimolar amount of diethyl ether and shaken for approximately 2 min. A molar equivalent of SnMe₄ was then added followed as quickly as possible by the monomer **1** such that its concentration in the reaction mixture was greater than 1.5 mol dm⁻³. Polymerization started immediately and the polymer was isolated, usually within 5 min, by dilution with chloroform followed by precipitation and washing in methanol followed by vacuum drying. Longer reaction periods, although resulting in nearly quantitative yields, produced insoluble polymer.

[‡] OsCl₃-catalysed reactions were carried out in sealed tubes at a catalyst/monomer ratio of 1:50 in a 1:1 chlorobenzene-ethanol mixed solvent at 65°C.⁷ In these experiments a chlorobenzene solution of monomer was added to an ethanol solution of catalyst such that the final monomer concentration was >3.0 mol dm⁻³. Polymer was isolated after 3 days by precipitation in methanol as above.

§ Spectra were taken in either CDCl₃ or C₆D₆ solution with SiMe₄ as internal standard.

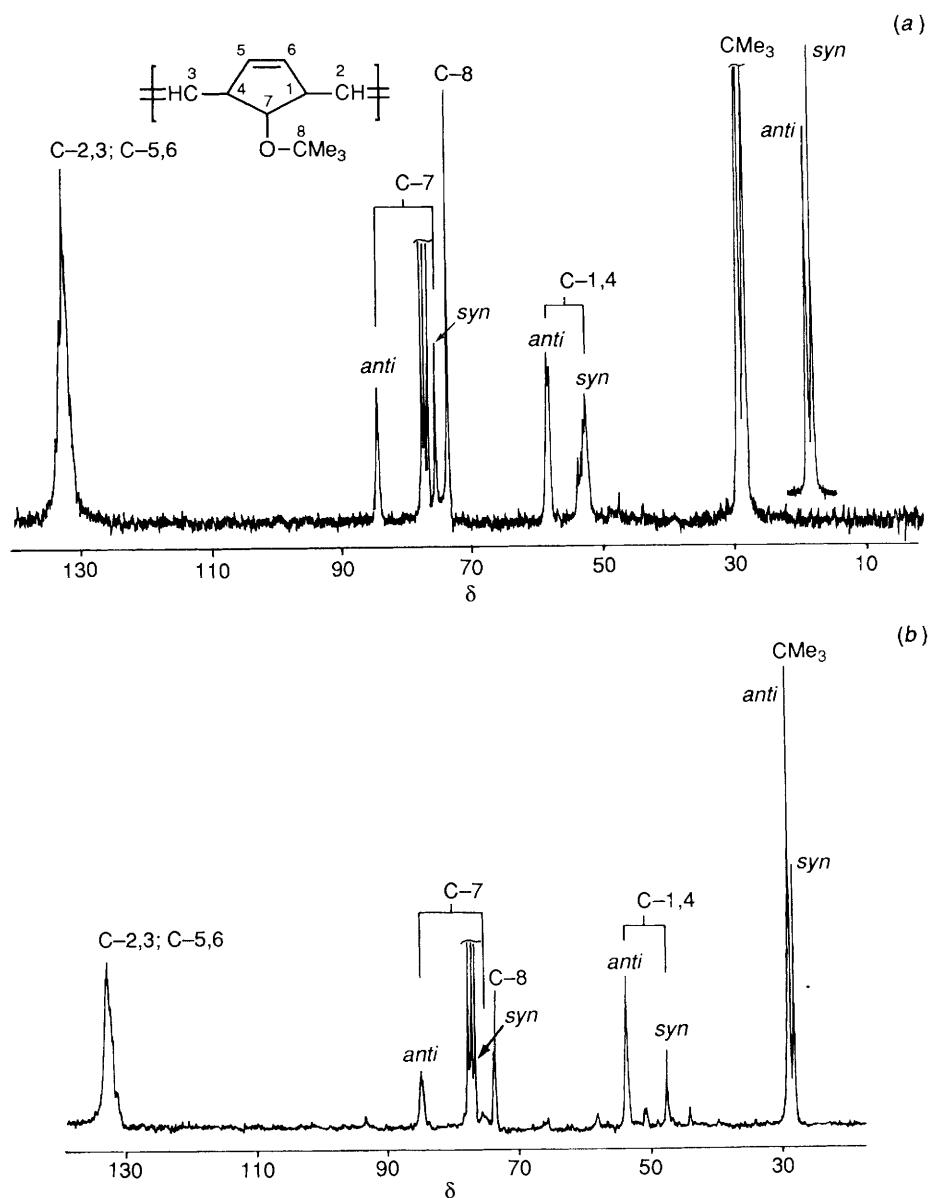


Fig. 1 ^{13}C NMR spectra (62.5 MHz) in CDCl_3 of, (a), polymer **2** prepared using the $\text{MoCl}_5\text{-SnMe}_4\text{-Et}_2\text{O}$ catalyst system and containing 60% *cis* main-chain double bonds and 56% *anti* units; (b), polymer of **2** prepared using the OsCl_3 catalyst and containing 100% *cis* main-chain double bonds and 75% *anti* units

The strong doublet (δ 28.36/29.11) for the methyl groups of the *tert*-butyl substituent is an intriguing feature. If it is assumed that *endo* attack does not occur and that *syn-exo* attack is strongly retarded or indeed prevented then only **2 anti** units (Scheme 1) would be found in the polymer chain.

Any fine structure would then have to be assigned to either *cis/trans* (*clt*) or tacticity (*mlr*) effects arising from neighbouring units in the polymer chain; this would, however, give rise to triplet fine structure (*cc, cltc, tt*) or (*mm, mlr/m, rr*) as found in the spectra of polymers of 7-alkylnorbornenes,¹ and not to the observed doublets. However, the *endo* face of NBD and its derivatives is much more accessible sterically than that of NBE. Furthermore, *syn-endo* attack as well as *anti-exo*, but not *syn-exo* are noted in the dihalocarbene addition reactions of **1** and its derivatives.⁸ We conclude, therefore, that the metallocarbene propagating species is also reacting here with the monomer in the *endo* as well as the *anti-exo* orientation. This would provide both *syn* and *anti* epimeric positioning of the 7-substituent in the polymer units. The orientation is almost nonspecific for the MoCl_5 -based catalyst so if *syn-exo* attack is excluded the *syn-endo* mode is just as likely as the sum of the *anti-exo* and *anti-endo* modes. There is no direct

experimental method of distinguishing between *exo* and *endo* attack but only between *syn* and *anti* units, **2** and **3**, for the present polymers. There is a bias in favour of *anti* epimeric positioning using the OsCl_3 based system (see below) and corresponding doublets are also found as expected for C-1,4 and C-7. The obvious and most likely explanation is that here the *anti-exo* mode of propagation is preferred over all others.

Establishing the *cis* double bond content in poly-(norbornadienes) is often a problem owing to the overlap of the alkenic lines.² An estimate of the *cis* content of **2** could, however, be made indirectly from the ^{13}C NMR spectra of copolymers of **1** and NBE since the signals from the NBE segments are easily identified. Thus, the MoCl_5 and OsCl_3 based systems yield *cis* double bond contents of 60 and 100%, respectively for the NBE homodyad units and we, therefore, conclude that homodyads from **1**, formed concomitantly have similar *cis* contents. This is consistent with the observation² that in the homopolymers of NBD and in copolymers with NBE made using the OsCl_3 catalyst all the double bonds are *cis* according to unambiguous direct assignment for all dyads. Furthermore, the intensity ratio and separation of the lines assigned to the *syn* and *anti tert*-butyl (methyls) do not change

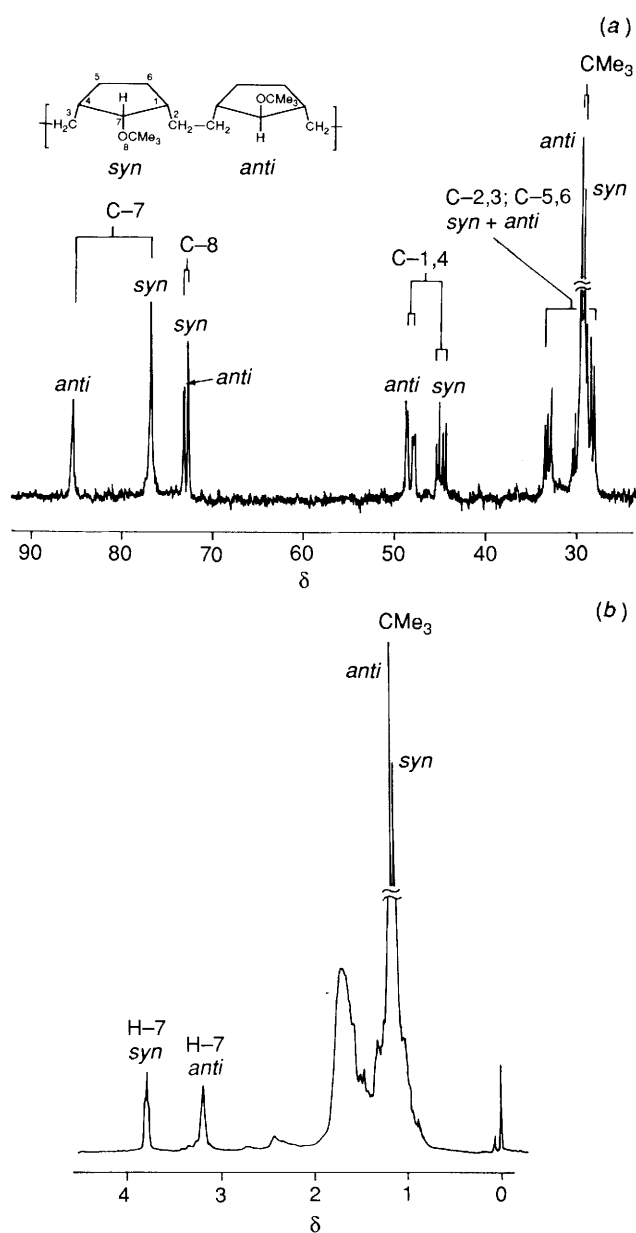


Fig. 2 (a) ¹³C NMR spectrum (125 MHz) in C₆D₆; (b) ¹H NMR spectrum (300 MHz) in CDCl₃ of hydrogenated polymer **3** derived from polymer **2**

as the NBE content in the copolymers with **1** increases to a large proportion where, statistically, homodyad units of **2** are no longer expected. Previous experience shows⁹ that analogous heterodyads give rise to large chemical shifts of the lines where the fine structure is due to *ct* or *mlr* effects.

The analysis of the microstructures is greatly clarified by consideration of the ¹³C and ¹H NMR spectra of the hydrogenated⁷ polymers **3**, Fig. 2(a) and (b). In these spectra any ambiguity which may arise from *ct* features is removed leaving only fine structure potentially attributable to the presence of **3**_{syn} and **3**_{anti} epimeric units or to ring tacticities. The ¹H NMR spectrum, Fig. 2(b), is particularly revealing. Here the H-7 methine proton appears as two broad singlets at

δ 3.2 and 3.8. The line at δ 3.2 is assigned to H-7 in the **3**_{anti} form and that at δ 3.8 to H-7 in the **3**_{syn} form based on unambiguous assignments for the analogous protons in epimers of *cis*-2,5-dimethylcyclopentan-1-ol and derivatives.¹⁰ The ¹H NMR spectra correlate well with the ¹³C spectra for both polymers **2** and **3**, Figs. 1 and 2, so the bias is clearly in favour of the *anti* mode of insertion of monomer units for the OsCl₃ catalyst. The OsCl₃ catalyst, therefore, seems to be more selective than the MoCl₅ catalyst in all aspects including *cis/trans*, *syn/anti* and even copolymer ratios.

The high *cis* content of the polymers made using the OsCl₃ catalyst shows that **1** also acts here as a di-*endo*-chelating spectator ligand crowding the reactive centre and forcing the metallacyclobutane transition state to adopt the less bulky *cis* orientation. This has also been noted in the polymerization of *endo*-dicyclopentadiene³ and NBD¹¹ so the effect observed here is consistent with the behaviour of this catalyst.

In our analysis of reaction rates and polymer microstructures consideration was given to a possible beneficial chelating effect on monomer reactivity arising from the lone pair on the oxygen atom and the *syn-exo* face of the double bond. We have previously found¹² that various 2,3-disubstituted derivatives of 7-oxanorbornadiene polymerized using the OsCl₃ initiator whereas the corresponding NBD derivatives failed to react. The present MoCl₃ based catalyst system was found to polymerize both types of monomer but the reaction is faster for the former class. This is in accord with the observation of Schrock *et al.*¹³ using a well-defined molybdenum carbene initiator. They attributed the beneficial effect of the 7-oxa substituent to such an *exo*-chelating effect, but we are now convinced that the lone pairs on the 7-oxygen atom repel the pairs of electrons of the double bonds away from the *exo* face thereby enhancing the ease of electrophilic attack on the *syn-endo* face by the carbene ligand of metallocarbenes with an $\overset{\delta+}{M}=\overset{\delta-}{M}$ dipolar orientation.¹⁴ Chelation may always be detrimental to rapid polymerization.

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