# Production of High-*trans* Isotactic Polymer of 5,5-Dimethylbicyclo[2.2.1]hept-2-ene using a Metathesis Catalyst

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A high-*trans*, isotactic polymer of 5,5-dimethylbicyclo[2.2.1]hept-2-ene can be prepared by ring-opening polymerization using (mesitylene)W(CO)$_3$–EtAlCl$_2$, activated by *exo*-2,3-epoxybicyclo[2.2.1]heptane, and working at low monomer concentration (0.4 mol dm^{-3}) in chlorobenzene solvent at room temperature.

We have shown elsewhere[1,2] that with some metathesis catalysts the ring-opening polymerization of 5,5-dimethylbicyclo[2.2.1]hept-2-ene (1) and related compounds[3] yields highly tactic polymers in which *cis*-double bonds are associated with syndiotactic (r) ring dyads and *trans*-double bonds with isotactic (m) ring dyads. The special case of an all-*cis*, fully syndiotactic polymer, may be represented by (2) (c = *cis*) and can be achieved by using ReCl$_5$ as catalyst. When made from a single enantiomer of (1) this polymer has a head–head (HH), tail–tail (TT) structure, as in (2). When
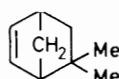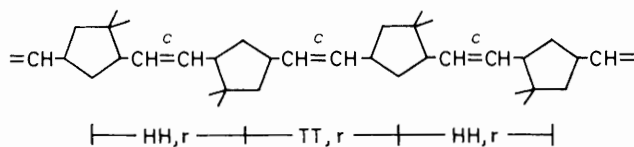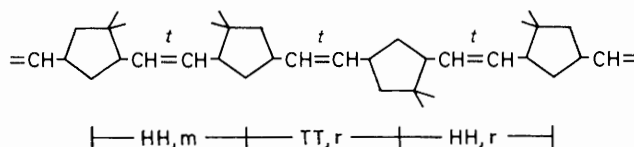
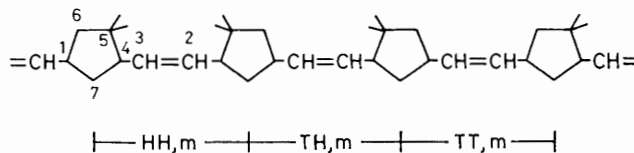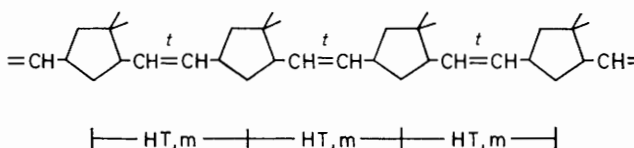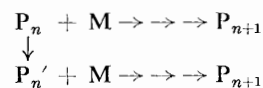made from racemic (1) the *gem*-dimethyl units are randomly disposed.

Other metathesis catalysts yield atactic polymers in which both *cis*- and *trans*-double bonds are associated with both m and r dyads.[1] For example RuCl$_3$ yields an all-*trans*-polymer in which there is only a slight bias in favour of m dyads relative to r dyads in the HH structures produced from racemic monomer; see (3) (t = *trans*). Until now, fully tactic polymers have always been of intermediate or high *cis*-content (σ_c = 0.5—1.0, where σ_c is the fraction of the double bonds which are *cis*). The catalyst used was (mesitylene)W(CO)$_3$–EtAlCl$_2$, activated with *exo*-2,3-epoxybicyclo[2.2.1]heptane[1] (4) and the polymer was prepared and analysed as previously described.[1] Using racemic monomer, the isotacticity of the polymer with respect to *trans*-double bonds is revealed by the absence of the olefinic C-3 resonance at 131.43 p.p.m. characteristic of the HH, r structure, while the peak at 131.14 p.p.m., due to HH, m, is present; see (5), and Figure 1(a) (*cf.* Figure 4 in ref. 1). The C-4 *trans*-resonance is also as expected for an isotactic dyad.[5] This is confirmed by the use of optically active monomer, which gives a predominantly HT structure (6) for *trans*-double bonds; Figure 1(b). As expected, the smaller proportion of *cis*-double bonds is associated with HH,TT (syndiotactic) dyad structures. These results show that it is possible to achieve an almost complete range of *cis*-contents (σ_c = 0.15—1.0) for fully tactic polymers as well as for semi-tactic or atactic polymers. As discussed elsewhere,[1,6] the formation of tactic polymers must involve propagation through chiral metallacarbenes, for example of pseudo-octahedral configuration [see (7)], with alternating enantiomeric forms associated with the formation of a *cis*-double bond, while the same enantiomeric form is repeated by the formation of a *trans*-double bond. On the other hand the formation of atactic polymer requires either that rupture of each metallacyclobutane may give both enantiomeric metallacarbenes, or that chiral identity of each product metallacarbene is always determined by the nature of its precursor metallacycle, but the enantiomeric forms then rapidly interconvert before the next propagation step.

The value of σ_c of the polymer obtained with the present catalyst system decreases from 0.40 when the monomer concentration [M] = 2.7 mol l^{-1} to 0.15 when [M] = 0.4 mol l^{-1}; also, as the monomer concentration is reduced, there is a slight tendency towards an HT bias in polymers made from racemic monomer (HH:HT:TT = 22:57:22 instead of 25:50:25 for a random orientation); see Figure 1(a).

The drop in σ_c and the emergence of HT bias with dilution of the monomer is in keeping with a relaxation of one chiral form of the propagating species P$_n$ to another form P$_n'$ of the same chirality. It is reasonable to suppose that the lower energy form P$_n'$ will be more discriminating in terms of both σ_c and HT bias. The nature of the initially formed species P$_n$

(1)

|— HH,r —|— TT, r —|— HH,r —|

(2)

|— HH,m —|— TT,r —|— HH,r —|

(3)

(4)

|— HH,m —|— TH,m —|— TT,m —|

(5)

|— HT,m —|— HT,m —|— HT,m —|

(6)

$$P_n + M \rightarrow \rightarrow \rightarrow P_{n+1}$$
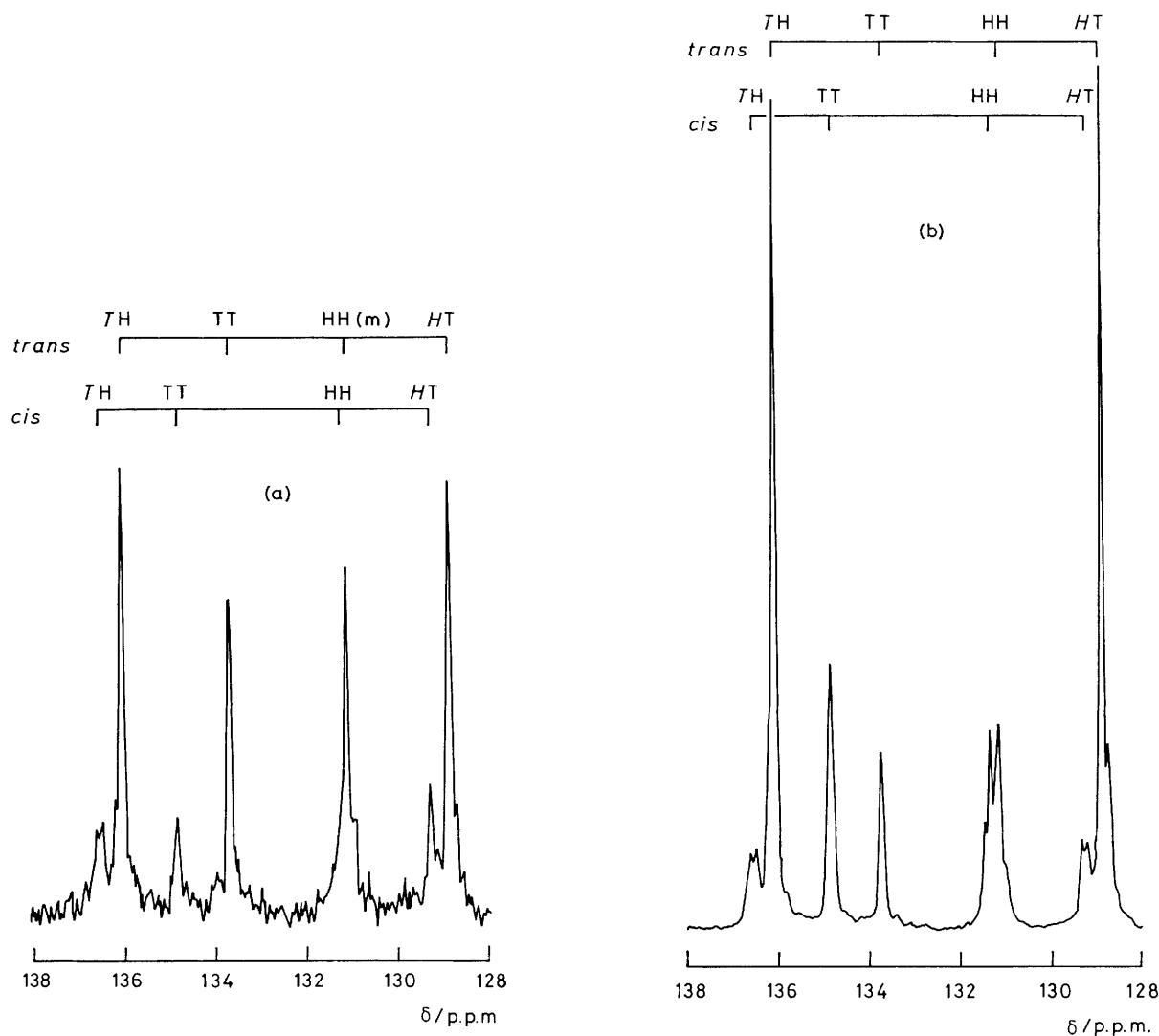$$\downarrow$$
$$P_n' + M \rightarrow \rightarrow \rightarrow P_{n+1}$$

Figure 1. 62.9 MHz $^{13}C\{^1H\}$ N.m.r. spectra (olefinic region) of polymers made from (a) racemic (1) and (b) optically active (1) (76% optical purity). Catalyst (mesitylene)W(CO)$_3$–EtAlCl$_2$–(4) (1 : 1 : 1). For (a) monomer concentration [M] = 0.4 mol l^{-1}, σ_c = 0.15; for (b) [M] = 2.7 mol l^{-1}, σ_c = 0.33.

and the relaxed form P_n' is a matter for speculation. One possibility is that P_n is the species in which the newly formed double bond is still co-ordinated to the catalyst site, while P_n' represents the species formed after deco-ordination. Such species have been postulated to explain the cis–trans distribution in high-cis-polymers of norbornene.[1] However in the present case we are observing effects at relatively low cis-content and it may be that both P_n and P_n' in this case are deco-ordinated forms but of different geometry. For example P_n could be the pseudo-octahedral form (7) while the more stable form P_n' is derived from it by a movement of the collinear CO and X ligands towards the vacancy □. Provided there is no rotation about the W=C bond the chirality will be preserved and the monomer will still prefer to approach the metal site in the same direction as for P_n but with a greater degree of selectivity, both with respect to orientation (governing the cis : trans ratio) and selection of enantiomers (governing the HT bias). Similar features have been observed[1] in polymers made using noble metal catalysts where the metallacarbenes seem to be much more stable than those of the metals of Groups 6 and 7 (less sensitive to water, alcohol, acids, etc.).

(7) (P_n)
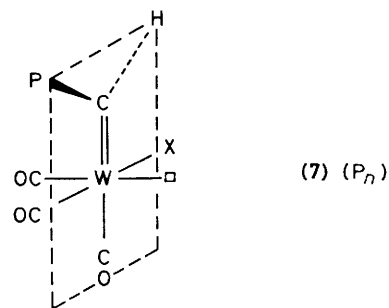
Recent work by Schrock et al.[7] has shown that tungsten alkylidene complexes in the absence of a strong π-donor ligand such as oxo or imido are highly distorted and, when the electron count is less than 18, may reversibly form an alkylidyne complex by transfer of the α-hydrogen atom to and from the metal. This process is tantamount to rotation of the alkylidene ligand and will rapidly interconvert left- and right-handed forms of the metallacarbene. While the oxo-alkylidene complexes of tungsten are essentially un-
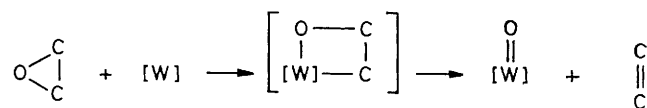
Scheme 1

distorted and do not undergo this hydrogen transfer, they are quite effective olefin metathesis catalysts.[8] The role of the epoxide in catalyst systems which give isotactic *trans*-dyads may therefore be to prevent this 'rotation' by placing an oxo-ligand on the active tungsten species [W] *via* intermediate formation and subsequent cleavage of the corresponding metallaoxacyclobutane (Scheme 1).

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