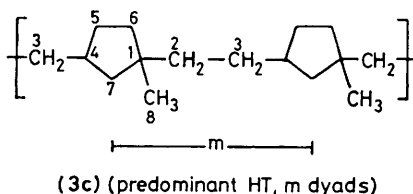


**Scheme 2.** Reagents: excess of *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NHNH<sub>2</sub>,<sup>6</sup> xylene, 110 °C, 1 h.

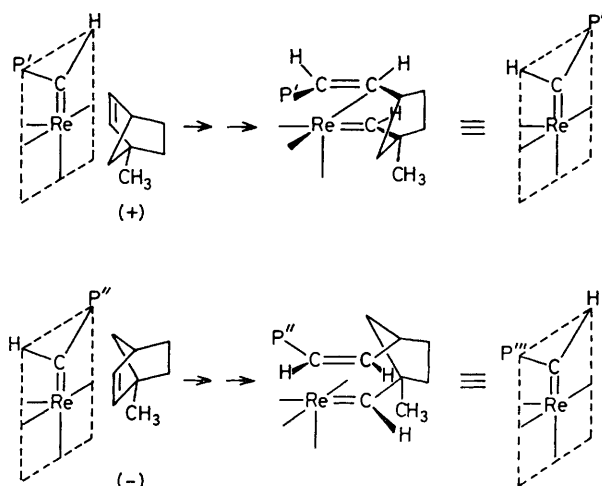
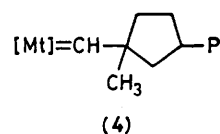


(1), OsCl<sub>5</sub>, 60 °C; and (c) optically active (1) (68% optical purity),<sup>5</sup> OsCl<sub>5</sub>, 60 °C, respectively. The <sup>13</sup>C n.m.r. spectra of the polymers (2b,c) show that the double bonds are all *trans* and that there is a strong bias towards an HT structure (HH: HT: TT *ca.* 1: 10: 1). The main lines (HT) may be unambiguously assigned: δ 139.34 (C<sup>2</sup>), 130.40 (C<sup>3</sup>), 47.77 (C<sup>7</sup>), 44.23 (C<sup>1</sup>), 42.10 (C<sup>4</sup>), 39.92 (C<sup>6</sup>), 32.47 (C<sup>5</sup>), and 27.09 p.p.m. (C<sup>8</sup>).

Polymer (3c), being made from optically active (1) *via* (2c), is obliged to have a predominantly isotactic dyad structure, as shown. The <sup>13</sup>C n.m.r. spectra of (3a,b,c) show a series of main lines emanating from the saturated HT units, which may be unambiguously assigned: δ 47.27 (C<sup>7</sup>), 42.92 (C<sup>2</sup>), 42.10 (C<sup>1</sup>), 39.79 (C<sup>4</sup>), 39.12 and/or 39.07 (C<sup>6</sup>), 32.46 (C<sup>3</sup>), 31.93 (C<sup>5</sup>), and 26.83 p.p.m. (C<sup>8</sup>). (3b) gives both C<sup>6</sup> lines, with approximately equal intensity, while (3c) gives only the 39.12 p.p.m. line and (3a) only the 39.07 p.p.m. line. A mixture of (3a) and (3b) gives both peaks, with the 39.07 p.p.m. peak enhanced. Since it is known that (3c) is predominantly isotactic we may assign the 39.12 p.p.m. peak to m dyads and hence the 39.07 p.p.m. peak to r dyads. Thus the polymer (3a), and its precursor (2a), must be essentially syndiotactic, as shown in Schemes 1 and 2. The C<sup>6</sup> m and r peaks in (3b), and its mixture with (3a), could only be resolved by operating the spectrometer (Bruker WM250) under optimum conditions (62.8 MHz, spectral width 6250 Hz, 32K free-induction-decay data points).

A consequence of the fact that ReCl<sub>5</sub> induces the alternating copolymerization of the two enantiomers of (1) is that it is likely to be difficult if not impossible to polymerize a single enantiomer of (1) with this catalyst. Indeed we did not succeed in polymerizing the monomer of 68% optical purity (84:16 ratio of enantiomers) with ReCl<sub>5</sub>.

The fact that the all-*cis* polymer is syndiotactic is well understood in terms of propagation by metal carbenes which have alternating chiral forms and where the reaction occurs at alternating *cis* ligand positions.<sup>1-3</sup> The fact that the polymer is all-*cis* is thought to be a consequence of strong co-ordination of the previously formed double bond at the Re site so that the propagation involves a displacement of this double bond by the incoming monomer in such a way as to lead to the formation of another *cis* double bond.<sup>1</sup> The fact that the ReCl<sub>5</sub>-initiated polymer has an all-HT structure may be attributed to the steric difficulty of forming the *cis*-1,2-disubstituted metallacyclobutane transition state that would be required to lead to a *cis*-HH dyad structure, both substituents being bulky quaternary groups. Without *cis*-HH dyads there can be no more than one *cis*-TT dyad per polymer chain in an all-*cis* polymer.



**Scheme 3**

Where there is a strong HT bias for dyads embracing *trans* double bonds, as for the OsCl<sub>5</sub>-initiated reaction, a different explanation must be given since there is no steric difficulty in forming a *trans*-1,2-disubstituted metallacyclobutane transition state. Indeed with other catalysts such as RuCl<sub>3</sub> there is no HT bias with respect to dyads containing *trans* double bonds. We propose that the extent of bias with respect to *trans* HT dyads is then governed by the polarity of the <sup>δ-</sup> C=C <sup>δ+</sup> bond. When this is strongly polar and in the direction indicated the electrophilic carbene moiety will seek the tail end of the double bond in the monomer (1), resulting in propagation through structure (4) and the repeated formation of HT dyads. The possibility that this type of polar effect is important in the case of ReCl<sub>5</sub> as well cannot be ignored. The strongly degenerate nature of the metathesis of *n*-alk-1-enes has been explained in a similar way.<sup>7</sup>

Although it has become customary to assume that the incoming olefin first co-ordinates and then reacts at the metal site the enantiomeric discrimination observed here implies that the C=C bond may react directly with [Mt]=C in a formal (2π + 2π) cycloaddition step to give a quasi-metallacyclobutane intermediate which then passes through a metallacyclobutane transition state.<sup>8,9</sup> The modes of addition essential to the production of the alternating copolymer (after displacement of the previously formed C=C from the Re site) are shown in Scheme 3, where P', P'', and P''' denote the polymer chain.

The alternating copolymerization of enantiomers observed with ReCl<sub>5</sub> as catalyst is clearly a consequence of a combination of steric factors, assisted by polar factors, leading to the formation of the syndiotactic, HT structure. We believe this to be the first example of alternating polymerization of enantiomers in polymer chemistry. There is, however, an interesting comparison to be drawn with the formation of syndiotactic, HT vinyl polymers where the reactive site chooses one of two prochiral faces of a single molecular form, in contrast with the present case where the reactive site chooses one of two enantiomeric forms having only one reactive face (*exo*).

Details of the procedures used in making the various assignments and a description of the structures of polymers of (1) made with other catalyst systems will be published elsewhere.

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