Formation of Ring-opened Syndiotactic and Atactic Polynorbornenes using Metathesis Catalysts; Evidence for Retention and Loss of Configuration of the Intermediate Metallocarbene

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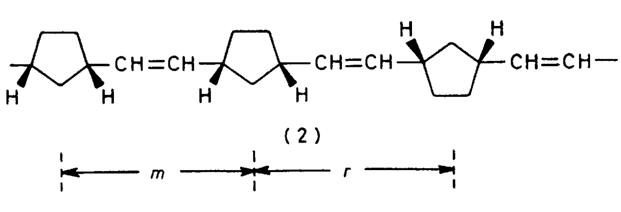
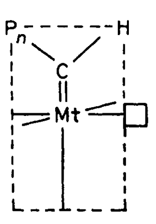
Summary All-*cis* ring-opened polymer made from (+)-*exo*-5-methylbicyclo[2.2.1]hept-2-ene (**1**) has a totally syndiotactic ring sequence whereas 11/89 *cis/trans* polymer is essentially atactic and 74/26 *cis/trans* polymer has mainly syndiotactic *cis* junctions and isotactic *trans* junctions; these results give information concerning the configurations of the propagating metallocarbenes in different catalyst systems.

IN the ring-opened polymers (**2**), obtained from bicyclo-[2.2.1]hept-2-ene (norbornene) using olefin metathesis catalysts, the double bonds may be *cis* or *trans*, and successive rings may stand in an *m* or *r* configurational relationship.[1] The two main-chain bonds attached to each ring are always *cis* with respect to one another.[2]

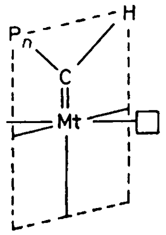


(**2**)

Polymerizations of this type are thought to be propagated by a metallocarbene chain carrier generated from the catalyst system.[3] If we denote a polymer chain with n monomer units by P_n, the transition metal by Mt, the vacant ligand position for co-ordination of the olefin by $\square$, and assume octahedral symmetry, then the metallocarbene may adopt any one of four conformations (**3**)—(**6**), about the metal–carbene bond, (**4**) and (**6**) being mirror images.



(3)



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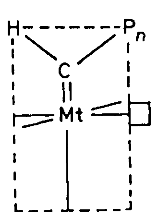

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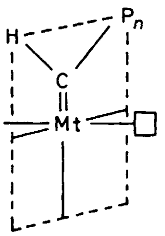
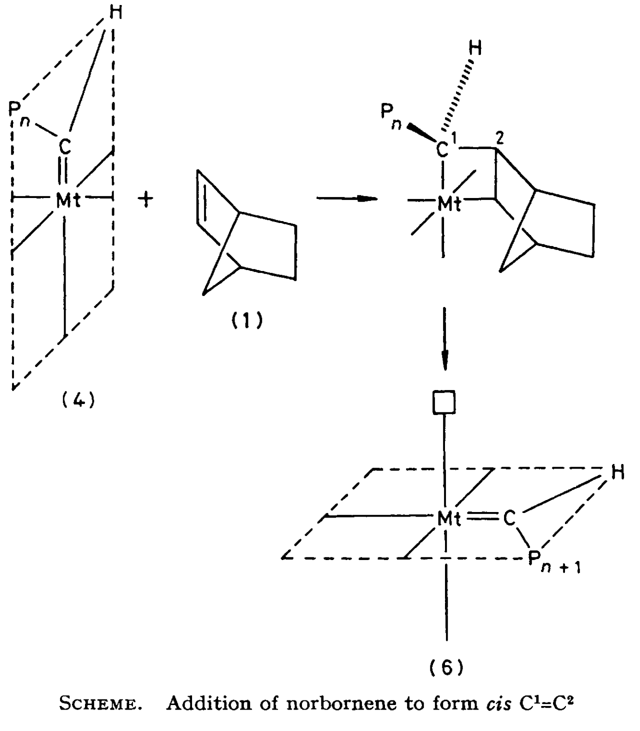


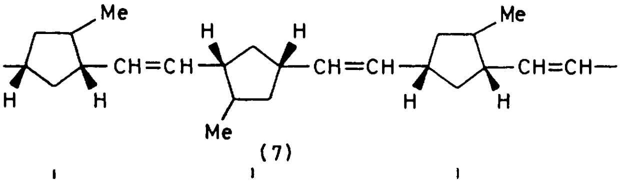
(6)

An unexpected feature of these polymers is that when the fraction of *cis* double bonds (σ_c) is high (0·5—0·9) the *trans* double bonds tend not to occur at random but in pairs, giving rise to a 'blocky' distribution.[4] This indicates that at high σ_c there are at least two kinetically distinct species, not at equilibrium, and we have argued[4] that these are likely to be (**4**) [≡(**6**)], and (**5**), which tend to add monomer to give *cis* and *trans* double bonds respectively. The preferred mode of formation of a *cis* double bond, by reaction of (**4**) with norbornene from the less hindered *exo* side, is then represented by the Scheme and the resulting metallocarbene has conformation (**6**). If the integrity of conformations (**4**) and (**6**) is preserved between additions of monomer then a syndiotactic ring sequence must result; otherwise the sequence will tend to be atactic.[1]



SCHEME. Addition of norbornene to form *cis* C^1=C^2

Direct determination of the ring tacticity from the ^{13}C n.m.r. spectrum of polynorbornene has proved impossible, the shift differences for *m* and *r* dyads being too small to be resolved.[5] We have shown how, in principle, the problem



(7)

may be solved by the use of an enantiomer of a 5-substituted norbornene.[5] Here we report the solution using compound (**1**). The method depends on the fact that a syndiotactic polymer of (**1**) will have the head-head (HH), tail-tail (TT) structure (**7**), while an isotactic polymer will have an HT

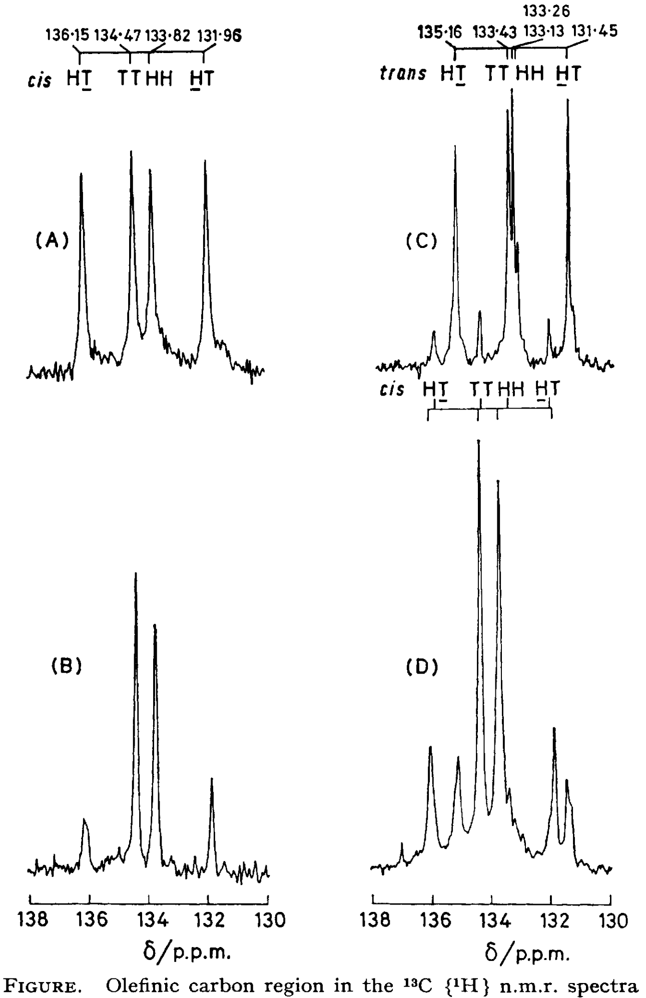


FIGURE. Olefinic carbon region in the ^{13}C {^{1}H} n.m.r. spectra (solvent $CDCl_3$) of polymers of (**1**) made under the following conditions (20 °C): (A) 0·486 g (±)-monomer, 7·2 mg $ReCl_5$, 0·25 cm^3 PhCl, 23·5 h, 71% yield; σ_c 1·0. (B) 0·510 g (+)-monomer, 9·0 mg $ReCl_5$, 0·3 cm^3 C_6H_6, 13·5 h, 100% yield; σ_c 1·0. (C) 0·457 g (+)-monomer, 3·1 mg Ru–cyclo-octadiene complex,[1] 2·0 cm^3 PhCl, 72 h, 15% yield; σ_c 0·11. (D) 0·523 g (+)-monomer, 17·6 mg Bu^{n}Sn–9·9 mg WCl_6–0·5 cm^3 C_6H_6 (premixed 15 min), 24 h, 49% yield; σ_c 0·74. (C) was obtained at 75 MHz; the rest at 22·63 MHz.

structure. Each structure gives rise to distinct resonances in the olefinic part of the ^{13}C n.m.r. spectrum, HH and TT giving one line each, and HT one for each of the two carbons. The line order (downfield to upfield) is H*T*, TT, HH, *H*T, *cis* and *trans* double bonds each giving rise to a set of four resonances.

The monomer was prepared by a route similar to that previously used for the (±)-*endo* compound,[5] the intermediate *exo*-5-carboxylic acid being separated from the *endo* acid by the iodolactone method[6] and resolved using cinchonidine.[7] The optical purity, best estimated from the peak heights in the all-*cis* polymer, was 73% (the intermediate impure *exo* acid gave a value of at least 58%). The monomer had $[\alpha]_D^{25}$ 17·8° (ethanol, *c* 6·15 g dl^{-1}).

The Figure shows the olefinic region of the spectra from four samples. Polymer (A) is an all-*cis* sample made from (±)-monomer. This is bound to have a random arrangement of methyl groups and accordingly gives four equally intense H*T*, TT, HH, *H*T lines. Polymer (B) is an all-*cis* sample made from (+)-monomer. The TT and HH lines are 3·3 times as strong as the HT lines and the latter are to be ascribed entirely to the presence of 13·5% (−)-enantiomer in the monomer and not at all to the presence of *m* dyads. Polymer (C) is an 11/89 *cis*/*trans* sample made from (+)-monomer. The spectrum consists essentially of four *cis* resonances [but in different positions from (A) because of the *trans* neighbours] and four equal *trans* resonances (with HH split into two). Polymer (D) is a 74/26 *cis*/*trans* sample in which the *cis* double bonds are clearly associated with predominantly *r* dyads and the *trans* double bonds with *m* dyads. Results with other samples show that (B), (D), and (C) are typical of the trend from tactic to atactic structures as σ_c decreases, all polymers with $\sigma_c < 0{\cdot}55$ being essentially atactic.

These results prove conclusively that for the all-*cis* polymer the conformations of successive propagating species must be mirror-images (so far as the relationships between P, H, and □ are concerned). The association of *trans* double bonds with *m* dyads under conditions of high σ_c is predicted by the theory.[1] The formation of atactic polymer at lower σ_c can be accounted for in several ways. Under these conditions either (a) (**5**) is the predominant carrier, or (b) (**3**)—(**6**) may have time to equilibrate by rotation[8] about Mt=C between successive additions of monomer, or (c) there may be ligand migration between successive additions of monomer, or (d) there may be a change of symmetry about Mt prior to monomer co-ordination. However it seems clear that high σ_c, blockiness, and stereoregularity stem from the same cause, namely steric crowding around the metal centre in an octahedral complex. These results may also have relevance to an understanding of stereoregularity[9] in the closely related field of Ziegler–Natta polymerization of α-olefins.

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