MECHANISM OF RING-OPENING POLYMERIZATION OF CYCLOALKENES INITIATED BY
METATHESIS CATALYSTS

Kenneth J. Ivin

Department of Chemistry, The Queen's University of Belfast, U.K.

Abstract - (+)-exo-5-methylbicyclo[2.2.1]-hept-2-ene has been prepared and
polymerized by ring-opening using a variety of metathesis catalysts.
$ReCl_5$ gives an all-cis polymer which is fully syndiotactic, as revealed
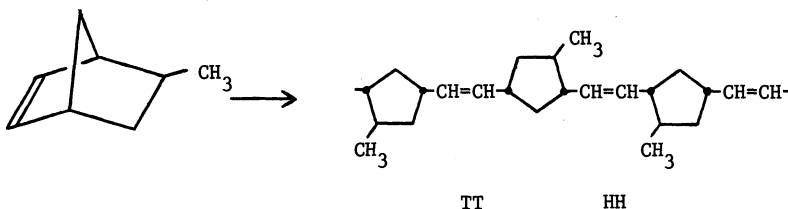

by the TT (tail-tail), HH (head-head) structure, identified by the
olefinic carbon resonances in the ^{13}C n.m.r. spectrum. $RuCl_3$-cyclo-
octadiene complex on the other hand gives a high-trans atactic structure
in which TT, HH, TH and HT occur to equal extents. These results indicate
that, under conditions leading to the all-cis polymer, intermediate
metallocarbenes of mirror-image types are formed alternately during
monomer addition, whereas under conditions leading to high-trans polymer
there is relaxation to a symmetrical form before every monomer addition.
The existence of two kinetically distinct propagating species accounts
for the blocky distribution of cis/trans double bonds when the cis content
is moderately high (> 50%); also for the variation of cis content with
preparation temperature in the polymerization of cyclopentene.

INTRODUCTION

There is now much evidence to substantiate the belief that olefin metathesis reactions
proceed by a chain mechanism in which the propagating species is a metallocarbene,
generated by the catalyst system, sometimes with the assistance of the substrate olefin.[1]

Stable metallocarbenes have been known[2] since 1964 and many have a six-coordinate structure.
The transient metallocarbenes involved in metathesis are harder to define with respect to
oxidation state of the transition metal Mt, the nature and number of permanent ligands, and
their spatial arrangement. Generally it has been assumed that the geometry about Mt (Ti,
V, Cr, Mo, W, Re, Os, Ir, Ru) is pseudo-octahedral, with one position occupied by the
carbene ligand and at least one position left vacant for coordination of the substrate
olefin.

In the ring-opening polymerization of a cycloalkene the propagating metallocarbene may be
represented as [Mt]=CHP where P is the polymer chain. In an octahedral complex the carbene
ligand may have one of four possible orientations[3] with respect to the vacancy ☐ , as
depicted in 1 - 4. 2 and 4 may be described as the mirror-image forms P_ℓ and P_r, and 1 and
3 as the symmetrical forms (referring of course only to the geometry defined by C-P, C-H
and ☐). Let us consider now how the metallocarbene mechanism applies to the ring-opening
polymerization of norbornene.

$$\underline{1} \qquad\qquad \underline{2} \qquad\qquad \underline{3} \qquad\qquad \underline{4}$$
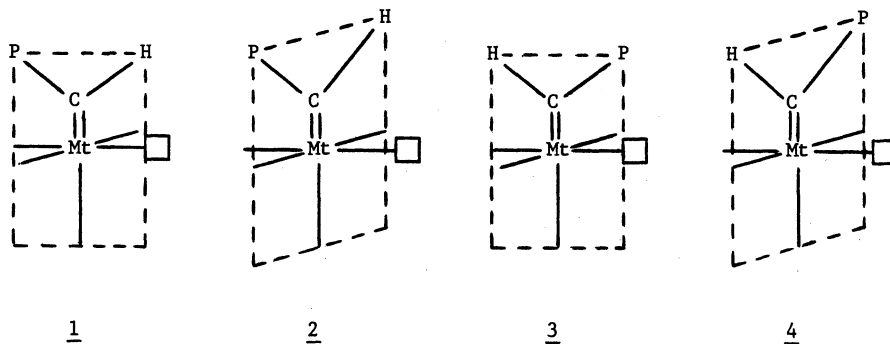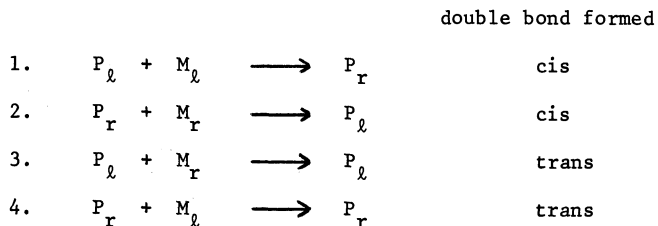
PREDICTION OF TACTICITY OF POLYMERS OF NORBORNENE

In the ring-opening polymerization of bicyclo[2.2.1]hept-2-ene (norbornene) it may be assumed that the monomer presents its less hindered exo side to the metallocarbene. The coupling of the monomer to the metallocarbene may occur in one of two ways according to which of the two olefinic carbons becomes attached to the carbene-carbon. The polymer chain may also have one of two positions so that altogether there are four possibilities,[4] of which one is represented in Scheme 1.

$$P_\ell + M_\ell \qquad\qquad\qquad\qquad\qquad\qquad P_r$$
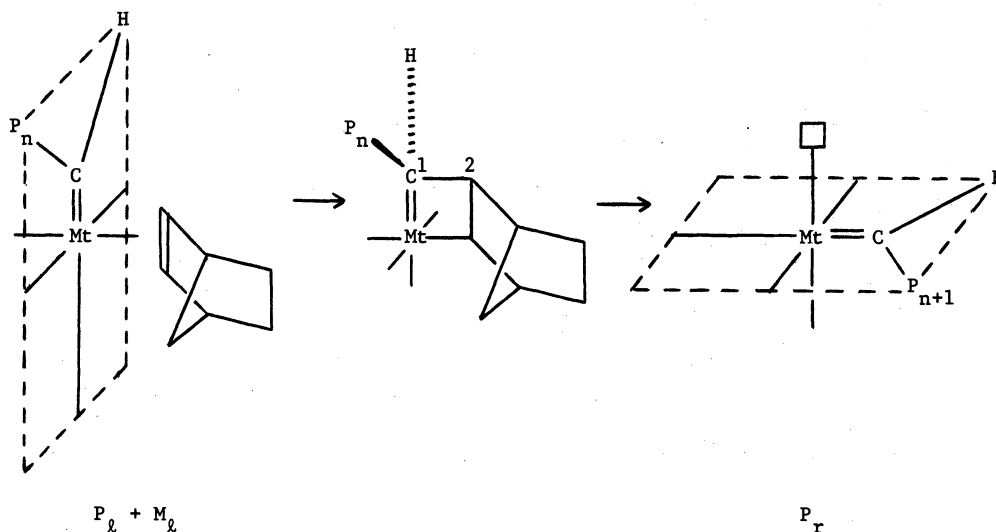
Scheme 1. Addition of norbornene, approaching Mt with the bridgehead carbon to the left (M_ℓ). Reaction with P_ℓ gives a cis double bond, $C^1{=}C^2$.
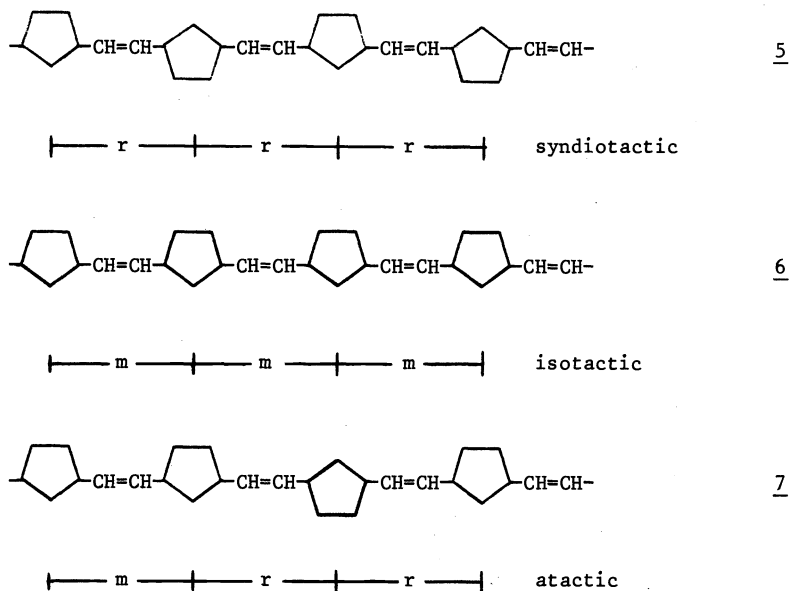
The product metallocarbene is likely to have the structure P_r but may also be the symmetrical structure $\underline{3}$. If for the moment we neglect the possible kinetic importance of $\underline{1}$ and $\underline{3}$ the growth of the polymer chain may be expressed in terms of the four propagation processes[4] shown in Scheme 2.

double bond formed

1. P_ℓ + M_ℓ $\longrightarrow$ P_r cis

2. P_r + M_r $\longrightarrow$ P_ℓ cis

3. P_ℓ + M_r $\longrightarrow$ P_ℓ trans

4. P_r + M_ℓ $\longrightarrow$ P_r trans

Scheme 2. Mechanism based on two structures of the metallocarbene and two modes of addition of monomer.

It should be noted that if the monomer molecule in Scheme 1 is turned over so that the bridgehead carbon is at the back (M_r), its addition to P_ℓ (process 3) results in the formation of a trans double bond and another P_ℓ-type metallocarbene.

The mode of addition of the monomer, M_ℓ or M_r, determines the configuration of the cyclopentane rings built into the chain. Successive rings may have a syndiotactic (r) or isotactic (m) relationship. The ring tacticity may be predicted from Scheme 2 assuming either (a) that the structures P_r and P_ℓ are preserved between addition of monomer molecules or (b) that they are racemized in some way. If the structures P_r and P_ℓ are preserved then an all-cis polymer can only be formed by the alternate occurrence of propagation processes 1 and 2. This means that the monomer molecules enter the chain alternately as M_ℓ and M_r giving the syndiotactic (r) sequence 5. Again if structures P_r and P_ℓ are preserved between monomer additions an all-trans polymer can result only by continuous repetition of process 3, or of process 4, and will have the isotactic (m) ring sequence 6. If on the other hand structures P_r and P_ℓ are racemized before every addition of monomer the ring sequence must be atactic, 7, regardless of the cis or trans double bond content.[5]

|———— r ————|———— r ————|———— r ————| syndiotactic   5

|———— m ————|———— m ————|———— m ————| isotactic   6

|———— m ————|———— r ————|———— r ————| atactic   7

METHOD FOR THE DETERMINATION OF TACTICITY IN POLYMERS OF NORBORNENE

In order to test these predictions it is clearly necessary to find some means of determining the tacticity. Unfortunately the ^{13}C n.m.r. spectra of the ring-opened polymers of norbornene do not show any fine structure which can be attributed to a tacticity effect. In order to solve this problem we have synthesized and polymerized (+)-exo-5-methyl-bicyclo[2.2.1]hept-2-ene.[6] If one were able to start from the pure enantiomer 8 a syndiotactic polymer would have the fully head-head (HH), tail-tail (TT) structure 9 while an isotactic polymer would have the fully tail-head (TH) structure 10. In an atactic polymer HH, HT, TH and TT structures would have equal probability, as though the polymer had been made from racemic monomer.
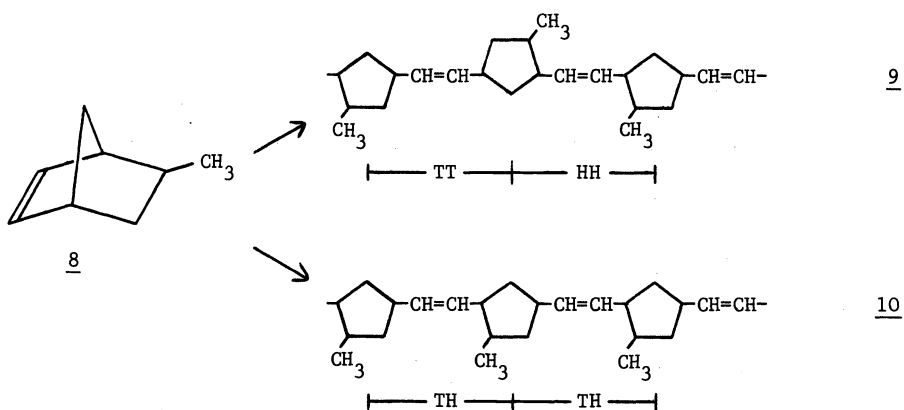
^{13}C chemical shifts are normally sensitive to substitution up to at least the δ position and one may therefore predict that these structures will have readily distinguishable olefinic resonances. Detailed considerations show that (a) the expected line order for the olefinic carbons (downfield to upfield) is HT, TT, HH, HT (the two distinguishable carbons in an HT structure are designated HT and HT), (b) the chemical shift difference for HT and TT will be very similar to that for HH and HT, and (c) cis and trans double bonds will each give a set of four lines, since the substitution parameters may be expected to be different in the two cases. These predictions have been entirely confirmed for both the endo-5-methyl[7] and exo-5-methyl[6,8] compounds. For example Fig. 1(a) shows the olefinic region for the all-cis polymer (initiated by $ReCl_5$) made from (±)-exo-5-methyl-bicyclo[2.2.1]hept-2-ene: the four peaks are well resolved, of equal intensity and have a symmetrical pattern. One can thus determine the tacticity indirectly by converting it to a head-head, head-tail, tail-tail effect.

RESULTS OF THE DETERMINATION OF TACTICITY

Fig. 1(b) shows the spectrum of an all-cis polymer made from (+)-monomer of estimated 73% optical purity. The TT, HH peaks are 3.3 times as intense as the HT, HT peaks. This pattern is consistent with a fully syndiotactic structure in which the outside peaks derive entirely from the presence of 13.5% (-)-enantiomer. The spectrum of a high-trans polymer (initiated by $RuCl_3$-cyclooctadiene complex) made from the same (+)-monomer is shown in Fig. 1(c) and is indistinguishable from the spectrum of a high-trans polymer made from racemic monomer. In this case the ring sequence is atactic even when the polymer is made from (+)-monomer. The fine structure of the HH peak is due to sensitivity of the chemical shift to the cis/trans structure of the next nearest double bond. Three of the four cis peaks may also be seen, but in positions slightly removed from those in the all-cis polymer, again because of sensitivity to the cis/trans structure of the next nearest double bond. Fig. 1(d) shows the spectrum of a 74/26 cis/trans polymer in which the cis double bonds are associated mainly with r dyads, and trans double bonds mainly with m dyads (the trans TT, HH peaks are weak and somewhat obscured by the cis HH peak).

DISCUSSION

These results provide clear proof that the production of all-cis polymer proceeds by way of alternate formation of P_l and P_r without any direct interconversion of P_l and P_r between addition of monomer molecules. On the other hand in the formation of high-trans polymer there must be total relaxation of the metallocarbene before every addition of monomer, either into equal proportions of P_l and P_r or into some symmetrical structure P_s which has an equal chance of adding monomer as M_l or M_r.

P_l and P_r will be kinetically indistinguishable if the four permanent ligands around Mt are the same but if they are different it would be possible, in principle, for P_l and P_r to have different reactivities and to react with monomer to give different cis/trans ratios. On the other hand a symmetrical structure P_s would almost certainly add monomer at a different rate, giving a different cis/trans ratio compared with the addition of monomer to P_l or P_r. P_s need not necessarily be octahedral (1 or 3) but may be square pyramidal or trigonal bipyramidal, with no formal vacant position.[5]

Two pieces of evidence indicate the undoubted presence of two kinetically distinct propagating species under certain conditions. First, we have shown that in polymers of norbornene having 35-80% cis double bonds the distribution of cis and trans double bonds is
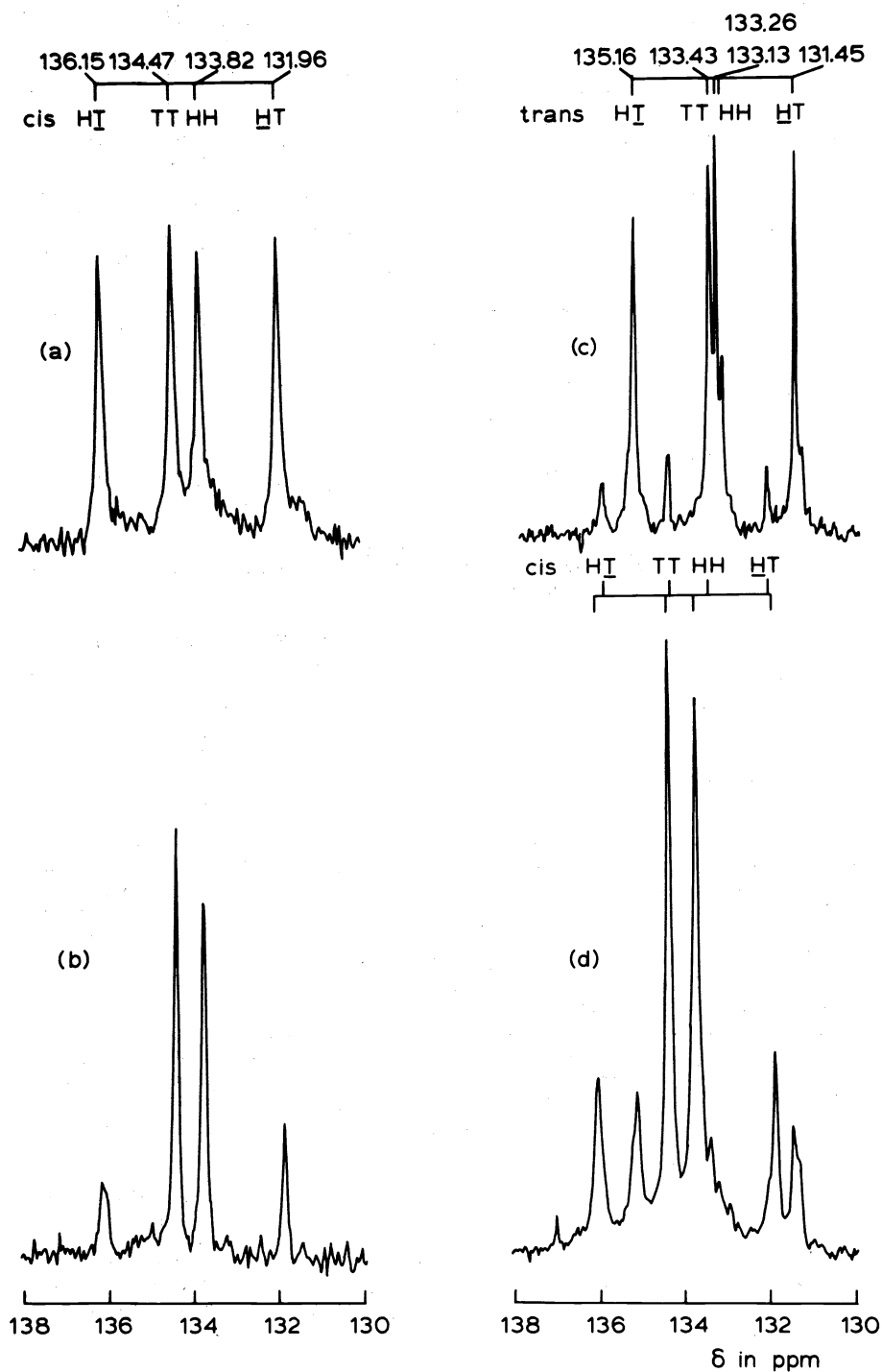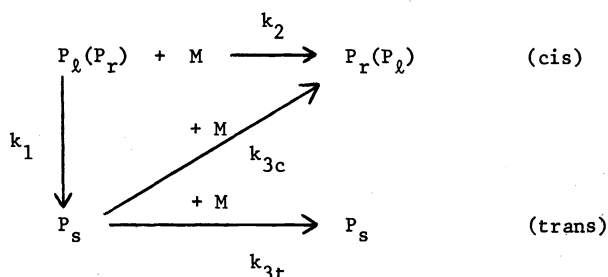
Fig. 1. Olefinic carbon region in the $^{13}C\{^1H\}$ n.m.r. spectra of polymers made by ring-opening of exo-5-methylbicyclo[2.2.1]hept-2-ene. (a) All-cis polymer made from (+)-monomer; (b) all-cis polymer made from (+)-monomer (73% optical purity); (c) 11/89 cis/trans polymer made from (+)-monomer; (d) 74/26 cis/trans polymer made from (+)-monomer. Reproduced with the permission of the Chemical Society from ref. 6.

distinctly non-random, in the direction of blockiness.[3] Representing the structure of pairs
of double bonds as tt, tc, ct and cc, we have shown that (tt)(cc)/(tc)(ct) > 1 when the cis
content is moderately high. This means that the chance of forming a cis or trans double
bond then depends on the structure of the previously formed double bond. For high-trans
polymers however the distribution of cis and trans double bonds is random, indicating total
relaxation to the same state before every addition of monomer.

The second piece of evidence concerns the variation of cis content of the polymer of cyclo-
pentene as the preparation temperature is raised. With $WCl_6/(CH_2=CHCH_2)_4Si$ as catalyst[9] the
cis content is close to 100% for temperatures between -80 and -30°C. Above this temperature
there is an abrupt fall until at 30°C the cis content is no more than 20%. Such behaviour
is entirely consistent with the mechanism shown in Scheme 3. Thus if the relaxation

$$P_\ell (P_r) \;+\; M \;\xrightarrow{\; k_2 \;}\; P_r(P_\ell) \qquad \text{(cis)}$$

$$P_\ell (P_r) \;\downarrow k_1$$

$$P_s \xrightarrow{\; +\,M,\; k_{3c}\;} \nearrow$$

$$P_s \;\xrightarrow{\; +\,M \;}\; P_s \qquad \text{(trans)}$$

$$k_{3t}$$

> Scheme 3. Propagation of polymerization of cyclopentene (M) via
> interconverting metallocarbenes P_ℓ, P_r and P_s.

process (k_1) is negligible at low temperature the propagation will proceed entirely via the
process represented by k_2. If $E_1 > E_2$ a temperature will eventually be reached where
$k_1 \gg k_2[M]$ and propagation will then proceed entirely by addition to P_s, so that if
$k_{3t} > k_{3c}$ the formation of trans double bonds will be favoured. A full analysis of the
data[5] gives $E_1 - E_2 = 55$ kJ/mol.

The main unresolved question is the nature of P_s and the mechanism by which it is formed
from P_ℓ and P_r. If P_s is octahedral, relaxation requires rotation about the metallocarbene
bond or ligand migration. If P_s is square pyramidal or trigonal bipyramidal only a change of
bond angles is required. The value of E_1 is likely to be in the region of 70-90 kJ/mol and
does not provide a means of distinguishing these possibilities. Thus the rotational barrier
about the metal-carbene bond is known to be of this order of magnitude in a tantalum complex
of tetrahedral symmetry.[10]

$ReCl_5$ and $Ph_2C=W(CO)_5$[11] presumably give all-cis polymers of norbornene because at room
temperature $k_1 \ll k_2[M]$. In keeping with this proposal we have found that dilution or
raising the temperature causes the cis content to fall off. With Ir- and Ru-based catalysts
the polymers are always atactic,[5,8] indicating $k_1 \gg k_2[M]$. The reason for the different
behaviour of the different catalyst systems is presumably connected with the extent of
d_π-p_π bonding of the ligands in the octahedral complex. The stronger this is the slower will
be the relaxation process, especially if it involves a change of symmetry.

CONCLUSIONS

There is good evidence that ring-opening polymerization of cycloalkenes involves at least
two types of active metallocarbene species which may interconvert during polymerization.
One type is chiral, probably octahedral, and adds monomer to give predominantly cis double
bonds; the other type is achiral but of uncertain symmetry and adds monomer to give mainly
trans double bonds. Certain catalysts propagate exclusively through the chiral species if
the temperature is low enough and/or the monomer concentration is high enough; with other
catalysts there is exclusive propagation through the achiral species.

REFERENCES

1. J.J. Rooney and A. Stewart, Chemical Society Specialist Periodical Reports on Catalysis
   1, 277 (1977).
2. E.O. Fischer and A. Maasböl, Angew. Chem. Int. Edn. 3, 580 (1964).
3. K.J. Ivin, D.T. Laverty, J.H. O'Donnell, J.J. Rooney and C.D. Stewart, Makromol. Chem.
   180, 1989 (1979).
4. K.J. Ivin, D.T. Laverty and J.J. Rooney, Makromol. Chem. 178, 1545 (1977).

5. K.J. Ivin, G. Lapienis, J.J. Rooney and C.D. Stewart, J. Mol. Catal. in press.
6. K.J. Ivin, G. Lapienis and J.J. Rooney, J. Chem. Soc., Chem. Commun. in press.
7. K.J. Ivin, D.T. Laverty, J.J. Rooney and P. Watt, Rec. Trav. Chim. Pays-Bas 96, M54
      (1977).
8. K.J. Ivin, G. Lapienis and J.J. Rooney, Polymer in press.
9. I.A. Oreshkin, L.I. Redkina, I.L. Kershenbaum, G.M. Chernenko, K.L. Makovetsky,
      E.I. Tinyakova and B.A. Dolgoplosk, Europ. Polym. J. 13, 447 (1977).
10. L.J. Guggenberger and R.R. Schrock, J. Amer. Chem. Soc. 97, 6578 (1975).
11. T.J. Katz, S.J. Lee and N. Acton, Tetrahedron Letters 4247 (1976).