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RING-OPENING POLYMERIZATION OF NORBORNENE CATALYSED BY $W(CO)_3Cl_2(AsPh_3)_2$ IN THE PRESENCE OF OTHER OLEFINS

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Summary

The steric course of ring-opening polymerization catalysed by $W(CO)_3Cl_2$-$(AsPh_3)_2$ is strongly influenced by the presence of other cyclic or linear olefins, such as cyclooctene, cyclohexene, 1-hexene and 1,7-octadiene. The blockiness of the polymer increases linearly with the overall olefin concentration in the reaction mixture. This effect of the individual olefins is independent of whether or not they participate in the cross-metathesis reaction to a detectable extent. The results are in agreement with the existence of two major kinetically-distinct propagating metallacarbene species, one *cis*- and one *trans*-directing.

Terminal olefins act as chain transfer agents. Based on polymer fractionation, ^{13}C NMR and GC-MS studies, two more kinds of selectivity of the catalyst was found besides the increase of σ_c and $r_c r_t$ of the polymer:

(i) The formation, exclusively, of oligomers of a nonsymmetric structure;

(ii) The lack of detectable products of the homometathesis of linear chain olefins.

The results are explained by the reluctance to form CH_2 carbenes and the relatively high reaction rate of propagation, chain transfer and degenerate metathesis, compared to the productive metathesis of the terminal olefins.

Introduction

$W(CO)_3Cl_2(AsPh_3)_2$ (I) is a single-component catalyst for the ring-opening polymerization of norbornene. The activity of the catalyst is not much affected by common catalyst poisons, such as water, alcohol, CO and oxygen, whereas the steric course of the reaction is somewhat variable [1].

In the present work we report an investigation on the course of norbornene polymerization initiated by I in the presence of other olefins.

Results

Polymerization of norbornene (NBE) occurs readily in benzene solution at 333–353 K in the presence of catalytic amounts of I under homogeneous conditions.

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TABLE 1
EXPERIMENTAL CONDITIONS

Run	[Norbornene] (mol l^{-1})	Co-olefin	[Co-olefin] (mol l^{-1})	[Catalyst] (mmol l^{-1})	Reaction time (h)	Yield of polymer (%)
1	0.07	–	–	7.01	6.0	80
2	0.25	–	–	2.56	0.33	29
3	0.50	–	–	9.96	1.0	25
4	2.96	–	–	5.84	0.33	48
5	1.13	1-Hexene	1.94	0.95	1.5	91
6	0.73	1-Hexene	3.30	1.63	1.0	70
7	0.78	1,7-Octadiene	1.24	0.96	6.6	64
8	0.78	1,7-Octadiene	1.24	0.96	2.5	42
9	0.41	Cyclooctene	1.48	1.61	1.4	34
10	1.13	Cyclooctene	1.36	1.48	0.33	33
11	0.46	Cyclohexene	5.13	1.82	1.0	30

The fraction of *cis* double bonds (σ_c) and the *cis/trans* blockiness ($r_c r_t$) of the ring-opened polymer appear to increase slightly with increasing monomer concentration (Tables 1 and 2). Since the solubility of the polymer is rather poor the yield is kept low by early gelation. Cross-metathesis with n-alk-l-enes was investigated as a means of controlling molecular weight and yields.

Linear olefins

When the polymerization was carried out in the presence of a somewhat less than two-fold mol excess of 1-hexene (NBE/1-hexene 1.72, run 5) in the starting reaction mixture no gelation occurred and nearly quantitative conversion of NBE was attained. On addition of ethanol, a large quantity of polymer precipitated (yield 73%) that was soluble in benzene and chloroform. ^{13}C NMR spectra of the product was typical of a ring-opened polymer from norbornene (Fig. 1a), however the σ_c and $r_c r_t$ values were somewhat higher than expected for an NBE homopolymer made in the absence of other olefins.

The benzene-ethanol soluble part of the reaction mixture was concentrated in vacuum, yielding a viscous liquid (yield 18%, $\overline{M}_n \sim 250$). The ^{13}C NMR spectrum of

TABLE 2
VALUES FOR *cis*-CONTENT (σ_c), REACTIVITY RATIOS (r_c AND r_t) AND BLOCKINESS ($r_c r_t$)

Run	σ_c	r_c	r_t	$r_c r_t$
1	0.52	1.4	1.4	2.0
2	0.54	1.1	1.0	1.1
3	0.54	1.5	1.9	2.9
4	0.58	2.6	1.4	3.6
5 [a]	0.58	2.6	2.2	5.4
6 [a]	0.56	3.0	1.8	5.4
7	0.56	1.8	2.2	4.0
8	0.58	2.6	1.8	4.7
9	0.51	1.1	2.2	2.4
10	0.62	2.9	1.5	4.3
11	0.57	3.1	2.3	7.1

[a] High molecular weight fraction.

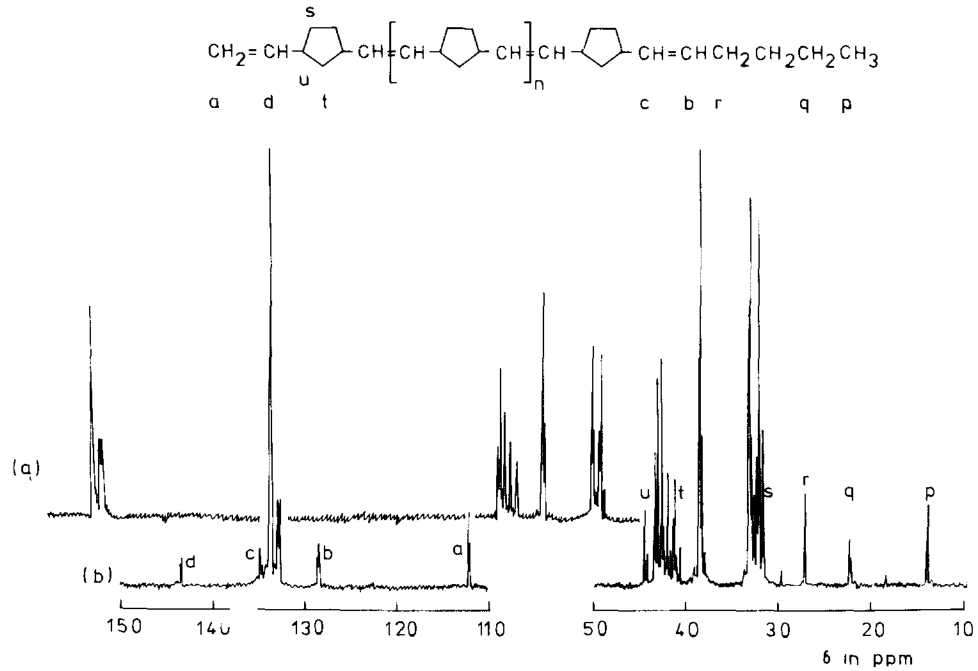
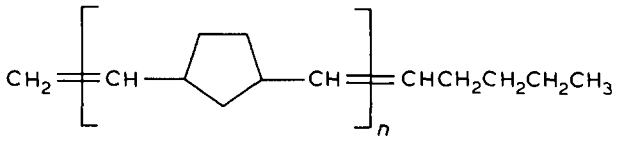


Fig. 1. ^{13}C NMR spectra of two poly(norbornene) fractions (in $CDCl_3$) isolated from run 6. (a) High molecular weight fraction, insoluble in benzene/ethanol (1 : 1) mixture. Yield 60%. (b) Benzene/ethanol-soluble fraction, $\overline{M}_n$ ~ 450. Yield 10%.

the sample is characteristic of a low molecular weight ring-opened norbornene polymer with CH_2= and =$CHCH_2CH_2CH_2CH_3$ end-groups (Fig. 1b).

It was found by GC-MS measurements that the end-groups have a non-random distribution, i.e. the ring-opened norbornene oligomers **A** have one methylene and one pentylidene end-group derive from the terminal co-olefin.



A

(n = 1,2,3,···etc.)

Symmetrical oligomers or homometathesis products (e.g. 5-decene) could not be detected in the reaction mixture.

When 1,7-octadiene was used as a co-olefin the result was analogous. When the reaction was terminated at 42% NBE conversion (run 8) with the addition of ethanol in a volume equal to the reaction mixture, the structure of the polymer precipitated (yield 37%, Fig. 2a) was definitely different from the benzene-ethanol soluble part (yield 5%, $\overline{M}_n$ ~ 2500; Fig. 2b).

The σ_c value for the latter is rather high (0.8). At higher NBE conversion (run 7) the molecular weight of the light fraction decreased sharply ($\overline{M}_n$ ~ 400; Fig. 3),

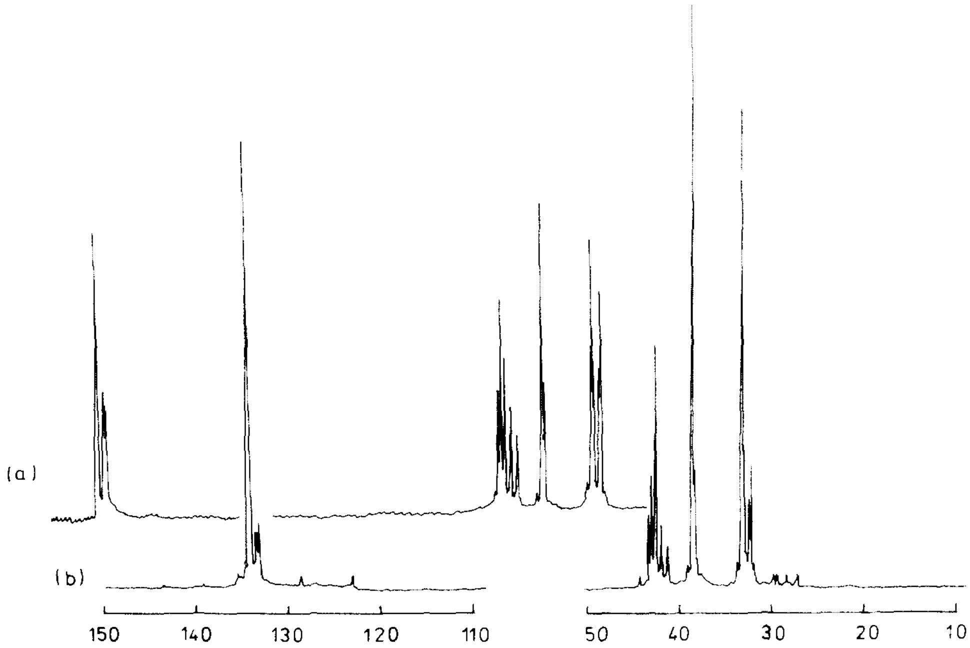
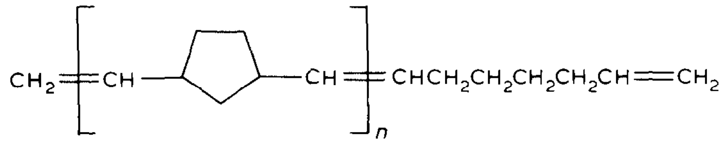


Fig. 2. ^{13}C NMR spectra of poly(norbornene) samples (in $CDCl_3$) isolated from run 8. (a) High molecular weight fraction precipitated from benzene/ethanol (1 : 1) mixture. Yield 37%. (b) Benzene/ethanol-soluble fraction, $\overline{M}_n \sim 2500$. Yield 5%.

while its quantity increased. All the oligomers have a non-symmetrical structure **B**.



B

Formation of symmetrical oligomers or homometathesis-products of the co-olefin such as cyclohexene, could not be detected.

Cycloolefins

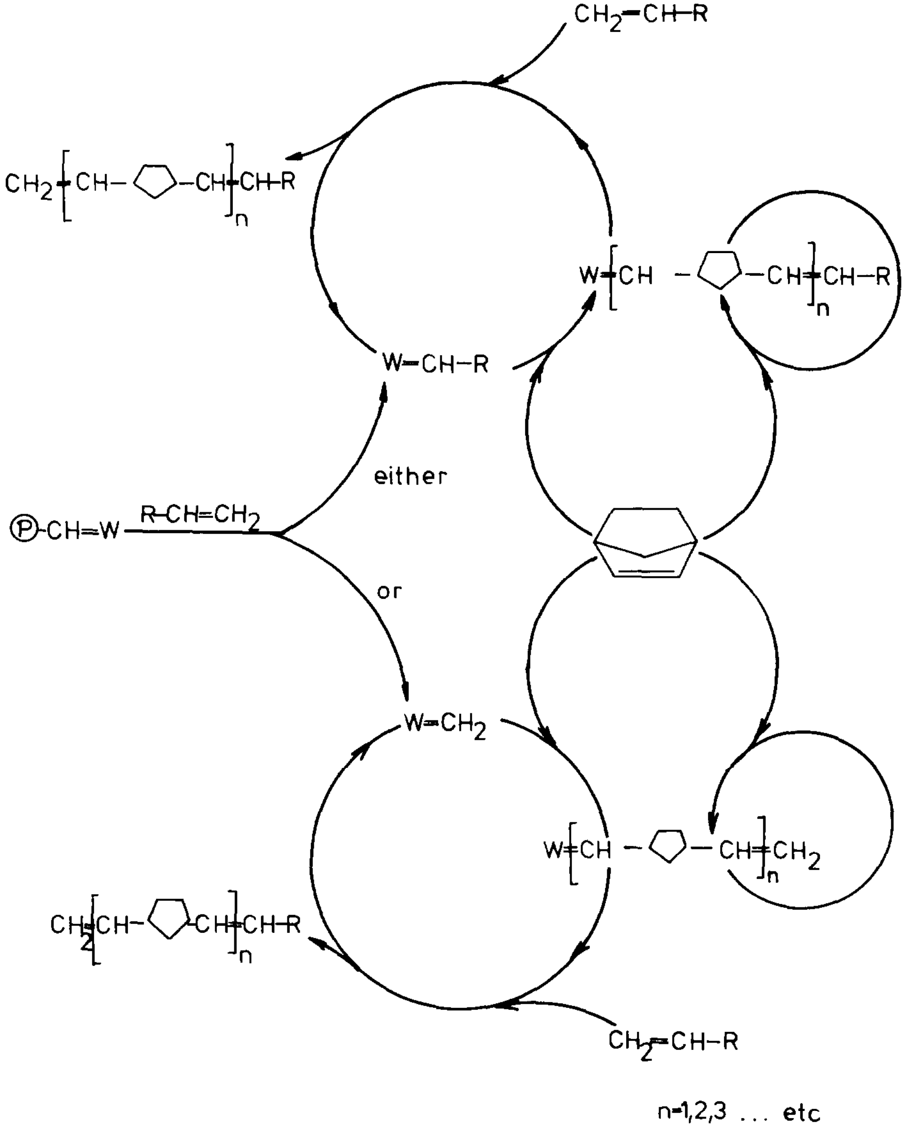
Incorporation of cyclooctene or cyclohexene into the norbornene polymer chain or their homopolymerization under the conditions studied could not be detected. However, their presence in the reaction mixture altered the steric course of the polymerization: an increase in *cis/trans* blockiness of the polymer was observed in every case (Table 2).

Discussion

In the reaction of I and NBE, active carbenoid species are formed that are able to initiate the ring-opening polymerization of norbornene. The presence of other, cycloor terminal, olefins in the reaction mixture influences the steric course of the polymerization, whether or not they are participating in the metathesis reaction.

It has been shown, that the chain-carrying polymer carbenes (Ⓟ-CH=W) are active enough to react with the terminal olefins which function as chain-transfer agents. However, the reaction is of very high selectivity in several aspects. All the polymers formed in this way are of a nonsymmetrical structure: one end of the chain is capped by a CH_2= group, while the other end is the corresponding alkylidene group derived from the terminal olefin. Oligomers with symmetrical end-groups (CH_2= or RCH= at both ends) could not be detected. This means, that the chain

SCHEME 1



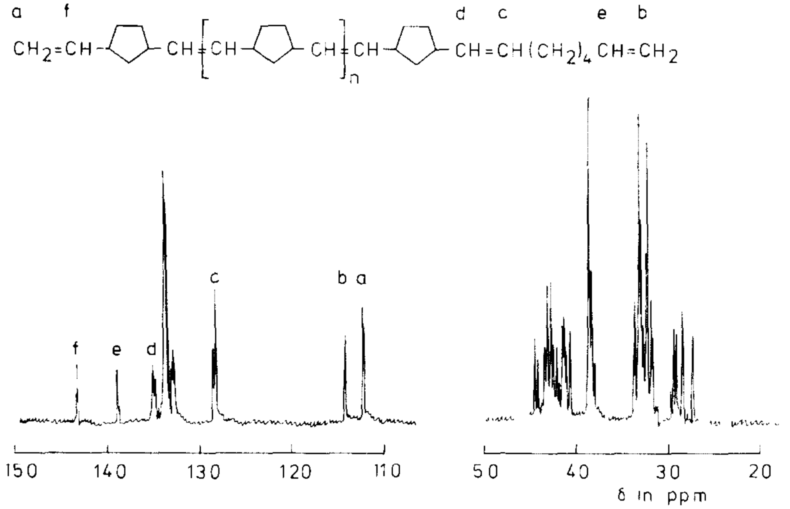


Fig. 3 ^{13}C NMR spectrum of a low molecular weight ($\overline{M}_n \sim 400$) high *cis* norbornene polymer with alkylidene end groups derived from 1,7-octadiene, in run 7. Yield 10%.

transferring metallacarbenes are identical throughout the reaction and they are regenerated in the chain-termination reaction (Scheme 1). Therefore, the kind of carbene formed from the terminal olefin must be either the W=CH$_2$ or W=CHR type, but by no means both in comparable amounts.

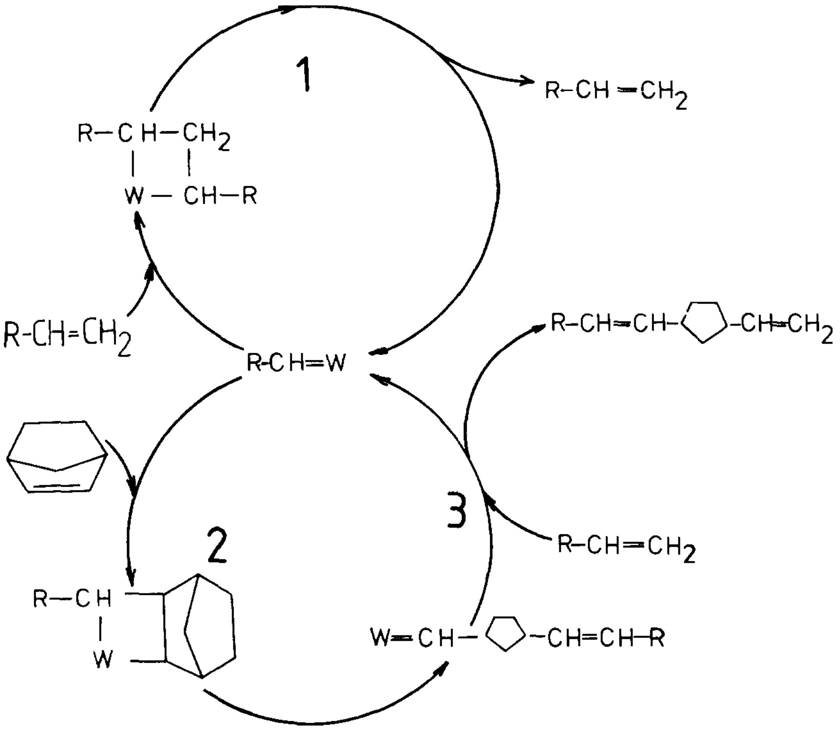
At this stage of the work we cannot tell which end-group comes from the initiating carbene and which is terminating the chain.

For some other tungsten-containing catalyst systems we concluded earlier that the probability of the formation of the CH$_2$= carbenes is rather small and most probably the RCH=W species are the chain-carrying carbenes in the unproductive metathesis of terminal olefins [2]. The lack of cyclohexene formation also points towards the absence of a W=CH$_2$ carbene; this explanation seems to be plausible here, too.

The exclusiveness of the formation of cross-metathesis products is another kind of selectivity exhibited by the catalytic system. Homometathesis products of the terminal olefins could not be detected. At high terminal olefin/NBE mol ratios, e.g. at the higher conversions (run 7, Fig. 3), the relative rate of propagation/transfer is about 3/1. This means that every fourth olefin reacting in a productive metathesis-like reaction is an acyclic one, and at least one of every fourth active species is a carbene derivative deriving from the acyclic olefin. This latter carbene is able to initiate the ring-opening polymerization of norbornene but apparently gives no productive metathesis with the terminal olefins.

This phenomenon cannot be explained on the basis of the hydrocarbon structures of the carbenes alone, because the chain-transferring RCH=W and the chain-carrying Ⓟ–CH=W carbenes are very much alike. Their reactivity should be more or less the same. The non-productive metathesis is known to be about two orders of magnitude higher than that of the productive one, and so the RCH= carbenes while staying in reaction course 1 are effectively unavailable for the productive metathesis, but are consumed much more rapidly in reaction 2 in Scheme 2.

SCHEME 2



Considering the large differences between the activity of NBE and the co-olefins, the incorporation of cyclohexene into the polymeric chain in detectable amount cannot be expected under the conditions studied. It is somewhat surprising therefore that the presence of the co-olefins influences the selectivity of the catalyst more than could be explained by the extent of their participation in the metathesis reaction.

As we reported earlier, the increasing concentration of the NBE, or the presence of other donor molecules (e.g. alcohol), increases the selectivity of the catalyst [1]. This sort of increasing selectivity has now been found in the presence of other olefins. In general, increasing the concentration of the co-olefin increases the σ_c and $r_c r_t$ values for the polymer. This effect is independent of whether the olefin is actually participating in the metathesis reaction or not. The experiments listed in Table 1 have not been specifically aimed at such an investigation; however it is apparent that the blockiness of the polymer is increasing more or less proportionally to the sum of the olefin concentration (see Table 2 and Fig. 4). Using the data of Tables 1 and 2, linear regression calculations were made to determine the probability of the existence of $Y = aX + b$ functions for $r_c r_t$ vs. [NBE] and $r_c r_t$ vs. Σ[olefin].

The linear regression coefficient (r) for the latter function was found to be 0.9, meaning that the $r_c r_t$ values are very probably linear functions of the sum of the olefin concentrations (Fig. 4). Similar calculation for the $r_c r_t$ vs. [NBE] gave a linear regression coefficient of $r = 0.14$, that is, there is a rather low probability for the existence of such a linear function in the presence of other olefins. Most of the multi-component catalysts used in laboratory practice for norbornene polymeriza-

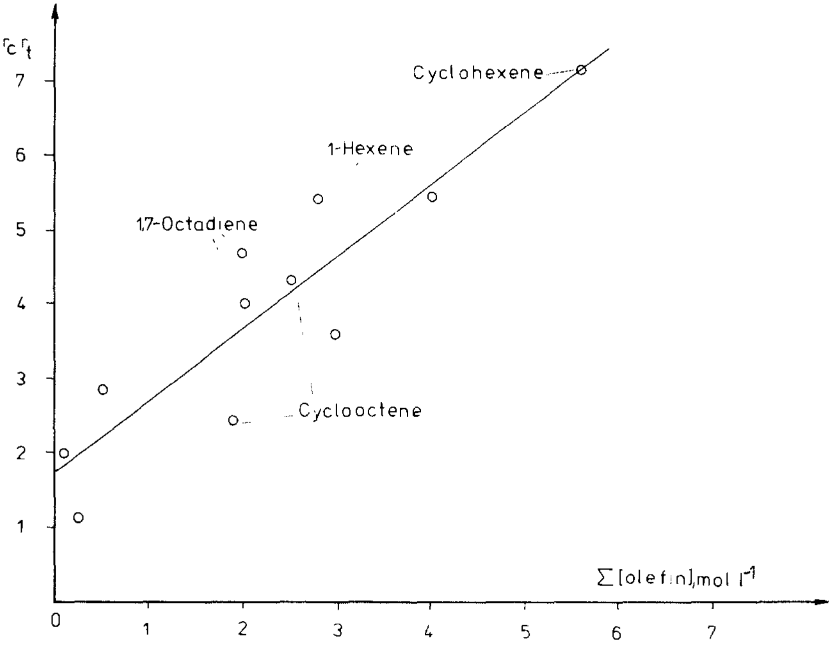


Fig. 4. Blockiness of the polymers ($r_c r_t$) plotted against the overall olefin concentration (Σ[olefin]). (The co-olefin is indicated, where one has been added.)

tion were found to be non-stereoselective. Rationalization of the *trans/cis* ratio of 1/1 is based mainly on the assumption that the metallacyclobutane intermediate in this case has an energy level lower than that of the coordinated olefin [3]. The studies were not extended to the examination of the distribution of the different stereoisomeric units along the polymer chain. Assuming that there is no orientation effect during the coordination of the monomer, a random distribution can be expected with alternating *-cis-trans-cis-trans-* sequences.

However, Ivin et al. [4,5] observed that in many cases the probability of the formation of a *cis* or *trans* double bond is influenced largely by the structure of the penultimately formed double bond, i.e. *cis* double bonds are followed by *cis* double bonds more frequently than expected for a random distribution; e.g. a polymer with $\sigma_c = 0.5$ might be composed of equal amounts of *-cis-cis-cis-* and *trans-trans-trans-* blocks. This phenomenon (termed blockiness [4]) cannot be explained by solely the relative stabilities of the intermediates.

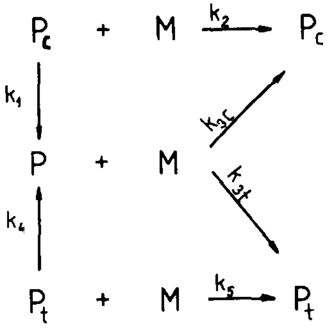
It has been postulated in several cases recently that the stereoselective feature of the catalysts, referred to as "formation of *cis* from *cis* and *trans* from *trans*" in the case of acyclic olefins and *cis/trans* blockiness in ring-opened polymers, can be accounted for by two kinetically distinct metallacarbene species, on *cis-* and one *trans*-directing [5–7].

The monomolecular $W(CO)_3Cl_2(AsPh_3)_2$ catalyst also has the tendency to form blocky poly(norbornene). This tendency is increased in the presence of other olefins. When cyclohexene is used as co-olefin, the *cis*-content of the polymer is not affected at all while the blockiness increases significantly.

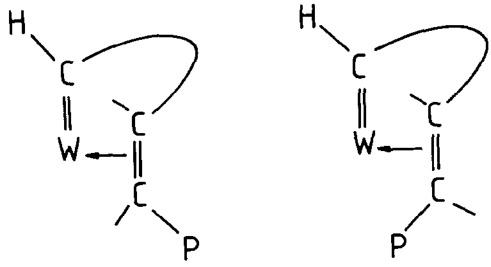
The overall structure of the polymeric product in run 11 may be described in terms of the repeating [*cis-cis-cis-cis-trans-trans-trans*]$_n$ sequence.

To get such a distribution, three kinetically distinct propagating species have to be considered, viz. P_c, P_t and P, and two relaxation process, $P_c \rightarrow P$ and $P_t \rightarrow P$, as shown in Scheme 3. P_c is a *cis*-directing propagating metallacarbene with which, in the complexation step, the norbornene is forced to react in the orientation which results again in *cis* double bond formation. P_t is the other main propagating species, forming mainly *trans* junctions (Scheme 4).

SCHEME 3



SCHEME 4



P_c P_t

The relative rate of formation of *cis* and *trans* junctions is not affected by the presence of cyclohexene, but that of the relaxation/propagation is.

One may speculate about the mechanism of the action of cyclohexene. There is little doubt about the cyclohexene being one of the ligands of the transition metal in P_c and P_t. The coordinated cyclohexene is an an asymmetric ligand. It may be blocking the access to one of the neighbouring coordination sites from one side and may also take part in a reversible metallocycle formation by "freezing in" the structure of the active species during the decoordination of the ultimately formed double bond and the coordination of a new norbornene molecule.

Formation of the species P in the given system is therefore hindered by the complexed cyclohexene, and the blockiness becomes a function of the cyclohexene concentration.

Experiments of ours are in progress to test these ideas.

Experimental

Hydrocarbons were dried and deoxygenated by refluxing over Na-K alloy/benzophenone and were distilled immediately before use.

All the manipulations were carried out in a dry argon atmosphere. The $W(CO)_3Cl_2(AsPh_3)_2$ catalyst was prepared as previously described [8].

The reactions were initiated by starting circulation of the preheated water or paraffin oil in the heating mantle of the all-glass reaction vessel. The reactions were terminated and the polymers precipitated by the addition of ethanol in a volume equal to the reaction mixture. The polymers were washed with ethanol and dried in vacuum. Oligomers were recovered from the benzene-ethanol solution by evaporating the solvents in vacuum.

Volatile products were identified by GC-MS analysis. ^{13}C NMR spectra were obtained as described in ref. 9. but with a reduced spectral window (4000 Hz). Calculation of σ_c, r_c and r_t was by the method of Ivin et al. [4], and based on the signals of the tertiary carbon atoms in the cyclopentane ring. Corrections for possible overlap of peaks was not attempted, because the errors were likely to be systematic. For details of the end-group analysis see ref. 10.

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