

# All *cis*-poly(NBE) derived by the ROMP catalysts based on $WCl_6$

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## Abstract

The ring-opening polymerization of bicyclo[2.2.1]-hept-2-ene (norbornene, NBE) is carried out with the metathesis catalysts  $WCl_6/RLi$ , where R = Me-, *n*-Bu-, *sec*-Bu-, *tert*-Bu-, *sec*-Bu<sub>x</sub>-C<sub>60</sub><sup>x-</sup>, *sec*-Bu-CH<sub>2</sub>-C(Ph)<sub>2</sub><sup>-</sup>, PS<sup>-</sup>. The bulkiness of the R chain of the co-catalyst, combined with the coordination of side substituents of R chain on the metal, increases the degree of *cis*-stereoselectivity of poly(NBE), beyond those of the systems based on  $WCl_6$  which are of intermediate *cis*-content. The range of the fraction of *cis*-double bonds varies from  $\sigma_c = 0.47$  to an all-*cis*-polymer ( $\sigma_c = 0.96$ ), and all the polymers derived exhibited a blocky distribution ( $r_c r_t > 1$ ) of the double-bond dyads. In case of R = PS<sup>-</sup> an all-*cis*-poly(NBE) was formed. The observed order for the *cis*-stereoselectivity is:

PS<sup>-</sup> > *sec*-Bu-CH<sub>2</sub>-C(Ph)<sub>2</sub><sup>-</sup> > *sec*-Bu- > *tert*-Bu- > *n*-Bu- > *sec*-Bu<sub>x</sub>-C<sub>60</sub><sup>x-</sup> > Me-

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## 1. Introduction

It is well known that ring-opening metathesis polymerization (ROMP) catalysts display a wide range of stereoselectivity in bicyclo [2.2.1]-hept-2-ene (norbornene, NBE) polymerization affording polymers whose steric configurations at the double bond, C=C, varies from nearly all-*cis* to nearly all-*trans*. The catalytic systems most commonly used are based on W, Re and Ru halide compounds. All-*cis*-polymers were produced from  $ReCl_5$  and all-*trans*-polymers were produced from  $RuCl_3$  [1]. Polymers of intermediate *cis*-content were produced from  $WCl_6$ -based systems [1,2]. One of the most common catalytic system based

on  $WCl_6$  is the  $WCl_6/n$ -BuLi first proposed by Wang and Menapace [3] in the metathesis reaction of 2-pentene. The same catalytic system was used by Ivin et al. in the ring-opening metathesis polymerization (ROMP) of norbornene with a mole ratio of  $WCl_6/n$ -BuLi ranging from 1/2 to 1/6 and the fraction of double bond having *cis*-structure,  $\sigma_c$  varying from 0.48 to 0.74, respectively [2]. Beyond the *n*-BuLi a series of co-catalysts have been used. Between them the most common is the  $WCl_6/SnR_4$  (R = Me, Et, Bu, Ph) [1].

As it is referred in literature the nature of R group of the  $WCl_6/SnR_4$  catalyst influences the stereoselectivity of polymers produced. In the polymerization of cyclopentene the catalytic system  $WCl_6/SnR_4$  for R = Me, gave  $\sigma_c = 0.2$  (+20 °C), for R = Et gave  $\sigma_c = 0.63$  (-10 °C), for R = Bu gave  $\sigma_c = 0.75$  (-10 °C), and for R = Ph gave  $\sigma_c = 0.88$  (-20 °C) [4]. Also, the same catalytic system at ambient temperature in

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the polymerization of norbornene for  $R = \text{Me}$  gave  $\sigma_c = 0.49$ , and for  $R = \text{Ph}$  gave  $\sigma_c = 0.60$  [5]. To all these systems the nature of R group forming the metal-carbene active center must be correlated with stereoselectivity. Kress et al. [6] for the metathesis reaction, reported that the activity and stereoselectivity of the well defined complexes  $\text{W}(\text{CHR})\text{L}_4$  changes with the L ligands and also changes with the structure of the R group in the order of  $R = \text{Me} > \text{Et} > \text{iPr}$ . These results are also consistent with Benzce's theoretical studies [7]. Recently, high *cis* (>90%) -polynorbornene was obtained using  $\text{WCl}_6/\text{SnMe}_4$  in dioxan [8], attributed to stereocontrol caused by the solvent.

According to Ivin's theory [2] among the most severe determining factors of selectivity of poly(NBE) which lead to the following *cis*-double bond formation:

- (a) Steric crowding at the metal center by ligands other than the olefin favors the orientation of complexed olefin and leads to *cis*-double bond formation.
- (b) The oxidation state of metal center. The higher oxidation state favors the formation of *cis*-double bonds [1,3,4].

In this work, we investigate extensively the influence of the substituent R of the metallocarbene for an increase of the *cis*-content of poly(NBE) carried out with  $\text{WCl}_6/\text{RLi}$  systems. The results related to the oxidation state of the metal center depend on the determining factors of selectivity referred above and are in agreement with Ivin's theory [2]. The stereoselectivity of the poly(NBE) until now produced with the  $\text{WCl}_6$ -based systems, was of intermediate *cis*-content, while our effort leads to an all-*cis*-poly(NBE). The catalytic systems used are based on  $\text{WCl}_6$  activated by the co-catalysts *n*-BuLi, *sec*-BuLi, *tert*-BuLi,  $\text{Bu-CH}_2\text{-C}(\text{Ph})_2\text{-Li}$ ,  $\text{PS-Li}$ ,  $\text{Bu}_x\text{-C}_{60}(\text{Li})_x$  ( $x = 6$ ),  $\text{SnMe}_4$  and MAO, where the R group is directly coordinated to the metal diminishing practically the role of the nature of the metal of co-catalyst.

## 2. Experimental

### 2.1. Materials

Organolithium compounds, *n*-BuLi, *tert*-BuLi, *sec*-BuLi,  $\text{SnMe}_4$  and  $\text{WCl}_6$  were purchased from

Aldrich Chemicals, methylalumoxane (MAO) from Witco, and used without further purification. Bicyclo[2.2.1]-hept-2-ene (norbornene, NBE) (Aldrich) and styrene (Aldrich) were refluxed over  $\text{CaH}_2$  and distilled under argon. Toluene was refluxed over metallic Na, distilled and stored under argon. 1,1'-Diphenylethylene (DPE) (Aldrich), was used as received. The  $\text{C}_{60}$  (>99% from TechnoCarbo) was kindly supplied by Dr. C. Mathis (Institut C. Sadron, CNRS, Strasbourg, France) and was stirred for several hours in pure THF and recovered by centrifugation. This procedure was repeated until the THF remained colorless. The  $\text{C}_{60}$  was then dried under vacuum at  $150^\circ\text{C}$ .

### 2.2. Polymerizations

All polymerizations were conducted at room temperature in a Schlenk tube under argon. The catalyst/co-catalyst ratio was in the range from 1/2 to 1/4 for the BuLi isomers, 1/1 for  $\text{Bu}_x\text{-C}_{60}^{x-}(\text{Li}^+)_x$  ( $x = 6$ ) and 1/2 for all the other co-catalysts used. The  $\text{WCl}_6$ /monomer ratio was 1/50.

In a typical polymerization procedure of NBE with the catalytic system  $\text{WCl}_6/\text{sec-BuLi}$ , 0.4 g ( $10^{-3}$  mol) of  $\text{WCl}_6$  were added to the flask followed by injection of 10 ml of toluene and 1.5 ml ( $2 \times 10^{-3}$  mol) of *sec*-BuLi (1.3 M). When the catalytic system was activated 4.7 g ( $50 \times 10^{-3}$  mol) of norbornene, dissolved in toluene, was injected. The reaction mixture instantly turned to dark brown and became viscous. The polymer was precipitated with excess of methanol. The precipitated polymer was collected, dissolved in a small amount of chloroform, and precipitated again as mentioned above. The methanol poured off and the polymer was dried under vacuum at  $50^\circ\text{C}$ .

### 2.3. Synthesis of butyl-1,1-diphenylethylenyl lithium ( $\text{Bu-CH}_2\text{-C}(\text{Ph})_2\text{-Li}^+$ )

The polymerization was carried out in a Schlenk tube under argon. A total of 10 ml of toluene was added to the flask followed by 1.6 ml ( $2 \times 10^{-3}$  mol) of *sec*-BuLi and 0.36 ml ( $2 \times 10^{-3}$  mol) of 1,1'-diphenylethylene (DPE) under efficient stirring. The color of the reaction mixture turns deep red which is characteristic of the diphenylethylene carbanions in toluene and was allowed to stir for 1 h.

#### 2.4. Synthesis of polystyryllithium ( $PS^-Li^+$ )

The polymerization was carried out in a Schlenk tube under argon. A total of 10 ml of toluene was added to the flask followed by 1.1 ml ( $1.3 \times 10^{-3}$  mol) of *sec*-BuLi. Then 4.4 ml of styrene was introduced to the Schlenk tube under efficient stirring. The color turns red–orange (yellow) which is characteristic of styrene carbanions in toluene. The reaction lasted for 2 h. After reaction, the solution of living anionic polystyrene species in toluene was divided in two parts. One was deactivated by methanol and characterized by GPC, the other was added to a toluene solution of  $WCl_6$ .

#### 2.5. Synthesis of $Bu_x-C_{60}^{x-}(Li^+)_x$ ( $x = 6$ )

A dark purple solution of 31.5 mg ( $0.04375 \times 10^{-3}$  mol) of  $C_{60}$  in 30 ml of toluene was prepared in a Schlenk tube, equipped with a magnetic stirrer, under argon atmosphere. After complete dissolution of  $C_{60}$ , 0.3 ml ( $0.35 \times 10^{-3}$  mol) of *sec*-BuLi (mol ratio *sec*-BuLi/ $C_{60} = 8/1$ ), with a gas-tight syringe, was injected. According to Ederle and Mathis [9] because of the stoichiometry of *sec*-BuLi/ $C_{60} = 8/1$  six butyl groups add on  $C_{60}$ . The excess of BuLi was used to kill any impurities. The color turns to dark-brown and the mixture was allowed to stir for 0.5 h.

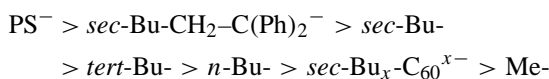
#### 2.6. Measurements

$^1H$  and  $^{13}C$  NMR spectra were obtained on a Bruker 250 MHz FT spectrometer operating at 250 ( $^1H$ ) and 62.89 MHz ( $^{13}C$ ).  $CDCl_3$  solvent provided the deuterium lock frequency. For  $^1H$  NMR spectra and  $^1H$ -decoupled  $^{13}C$  spectra the conditions and the procedure of calculations were those described by Ivin et al. [2]. The results obtained by  $^{13}C$  and  $^1H$  NMR on the same sample gave the same value for the percent of *cis*-double bonds. GPC data were obtained using a Waters Associates 401 Liquid Chromatography apparatus equipped with both, a Varian UV-50 detector and a differential refractometer detector. The eluent was  $CHCl_3$  and ultrastyrigel HR3 and HR2 columns in series were used. Molecular weight calibrations were run against a polystyrene standard. ESR spectra were performed on a Varian E-109 spectrometer at room temperature. The *g*-values were estimated using 1,1-diphenyl-2-picrylhydrazyl (DDPH) as reference.

### 3. Results and discussion

#### 3.1. The polymerization of NBE with the catalytic system $WCl_6/RLi$

According to Ivin's theory [2] poly(NBE)'s with fraction of *cis*-double bond,  $\sigma_c$  up to 0.35, showed random distribution of *cis*- and *trans*-structures ( $r_c r_t = 1$ ) while polymers having  $\sigma_c = 0.35$ –0.85 showed blocky distribution ( $r_c r_t > 1$ ) with  $r_c r_t$  values  $> 5$  in some cases. Also an increase of  $\sigma_c$  increases or reduces  $r_c$  and  $r_t$  values, respectively. For the interpretation of these results it was proposed that steric crowding of the active sites leads both to high values of  $\sigma_c$  and to restriction of rotation about the metal–carbene bond of the propagating metallocarbene species. This gives rise to kinetically distinct conformations which tend to regenerate their own kind on addition of monomer. The fraction  $\sigma_c$ , of *cis*-double bond, the reactivity ratios,  $r_c$  and  $r_t$ , and  $r_c r_t$  values ( $r_c r_t = 1$  and  $r_c r_t > 1$  correspond to random and blocky distributions of *cis*- and *trans*-double bonds, respectively) in the polymerization of NBE with the catalytic system  $WCl_6/RLi$  are shown in Table 1. Values  $r_c$  and  $r_t$ , express the distribution of the *cis* (*c*)- and *trans* (*t*)-double bonds in the polymer chain:  $r_c = tt/tc$ ,  $r_t = cc/ct$  [10]. As it is seen from this table the catalytic systems used gave:  $0.49 < \sigma_c < 0.96$  (all-*cis*-poly(NBE)) and  $r_c r_t > 1$ . Plots of  $r_c$ ,  $r_t$  and  $r_c r_t$  against the fraction,  $\sigma_c$  of double bonds having *cis*-structure are shown in Fig. 1. As it shown in Fig. 1 the dependence of  $r_c$ ,  $r_t$  and  $r_c r_t$  on  $\sigma_c$  is consistent with Ivin's theory for the *cis*- and *trans*-directing metallocarbene species. The existence of *cis*-directing species, derived by the catalytic systems used, seems to be based on steric crowding of R group in the beginning of the reaction. This is also consistent with Kress's [6] and Benzce's [7] experimental and theoretical studies mentioned before. As it comes out from  $\sigma_c$  values (Table 1) the observed order of *cis*-selectivity is:



The order of *cis*-selectivity parallels the order of bulkiness of R group. But two defects are observed. The first is with the  $sec-Bu_x-C_{60}^{x-}$  group which

Table 1

Microstructure of the poly(1,3-cyclopentylenevinylene)'s obtained with  $WCl_6$ -based catalytic systems

Run	Catalytic system	$\sigma_c$	$r_c$	$r_t$	$r_c r_t$	Type of double bond distribution
1	$WCl_6/n\text{-BuLi}$ (1/2)	0.54	1.80	1.39	2.50	Blocky
2	$WCl_6/sec\text{-BuLi}$ (1/2)	0.62	2.95	1.47	4.34	Blocky
3	$WCl_6/tert\text{-BuLi}$ (1/2)	0.56	1.97	1.35	2.65	Blocky
4	$WCl_6/n\text{-BuLi}$ (1/4)	0.68	4.34	1.52	6.60	Blocky
5	$WCl_6/sec\text{-BuLi}$ (1/4)	0.71	4.60	1.32	6.07	Blocky
6	$WCl_6/tert\text{-BuLi}$ (1/4)	0.69	4.29	1.43	6.13	Blocky
7	$WCl_6/Bu\text{-CH}_2\text{-C(Ph)}_2\text{Li}$ (1/2)	0.80	7.05	1.02	7.19	Blocky
8	$WCl_6/sec\text{-Bu}_x\text{-C}_{60}(\text{Li})_x$ ( $x = 6$ ) (1/2)	0.52	1.56	1.38	2.15	Blocky
9	$WCl_6/PSLi$ (1/2) <sup>a</sup>	0.96	—	—	—	Blocky
10	$WCl_6/MAO$ (1/1.5)	0.49	1.37	1.48	2.02	Blocky
11	$WCl_6/SnMe_4$ (1/2)	0.47	1.40	1.71	2.39	Blocky
12	$WCl_4$	0.81	8.5	1.24	10.54	Blocky

<sup>a</sup> In polymers with  $\sigma_c = 0.85\text{--}1.00$ , the  $r_c r_t$  value is difficult to determine because of the  $ct$  peak becomes lost in the side of the  $cc$  peak in the  $cis$ -olefinic region [2]. All polymerizations were carried out in ambient temperature and finished in few minutes. In all cases consumption of monomer was 100% except in cases of  $WCl_4$  and  $WCl_6/sec\text{-Bu}_x\text{-C}_{60}(\text{Li})_x$  finished in 16 and 2 h and yield of polymer produced was 16 and 45%, respectively.

should be after  $sec\text{-Bu-CH}_2\text{-C(Ph)}_2^-$  and before  $sec\text{-Bu-}$ . The second is between the BuLi isomers.

Let us first examine the case of  $sec\text{-Bu}_x\text{-C}_{60}^{x-}$  ( $x = 6$ ) group. This result is really surprising because a bulky substituent as the  $sec\text{-Bu}_x\text{-C}_{60}^{x-}$  does not lead to high  $cis$ -content of poly(NBE). This, is explained by the very crowding environment which surrounds the  $W\text{-C}_{60}$  coming as it is shown in Scheme 1a and b, from the star architecture of  $sec\text{-Bu}_x\text{-C}_{60}^{x-}$

$W_x(\text{Cl}_5)_x$  ( $x = 6$ ). This effect works to the opposite direction because it makes difficult the insertion of the monomer to the bond  $W\text{-C}_{60}$ . The reaction is not fast, the yield falls, and the monomer insertion facilitates

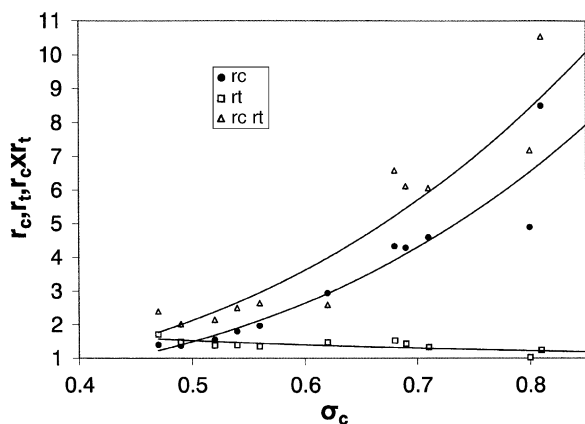
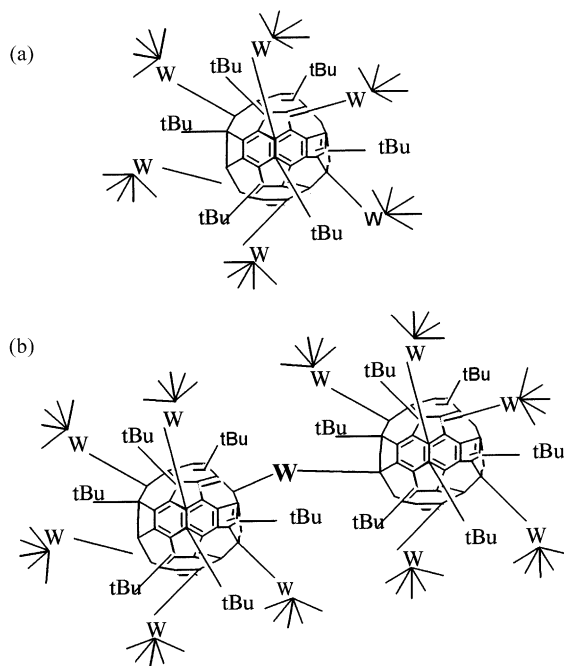


Fig. 1. Plots of  $r_c$  (●),  $r_t$  (□) and  $r_c r_t$  (Δ) against the fraction of double bonds having  $cis$ -structure,  $\sigma_c$  for  $WCl_6/RLi$ -based systems. Values of  $r_c$ ,  $r_t$  and  $r_c r_t$  are shown in Table 1.



Scheme 1.

the formation of a *trans*-intermediate. The formation of the  $\text{sec-Bu}_x\text{-C}_{60}^{x-}\text{W}_x(\text{Cl}_5)_x$  is evaluated through the addition of BuLi on  $\text{C}_{60}$ . There are six symmetrical places on the buckminsterfullerene ( $\text{C}_{60}$ ) for the addition of BuLi. The addition of BuLi forms six symmetrical,  $\text{C}_{60}^{6-}(\text{Li}^+)_6$  ion pairs [9]. In this ion pair bond the  $\text{WCl}_6$  is added forming the W–C bond. The six symmetrical W–C bonds present the same possibility for an endo- or exo-addition of norbornene forming equal amounts of *trans*- and *cis*-double bonds. The detailed study of these species is in progress.

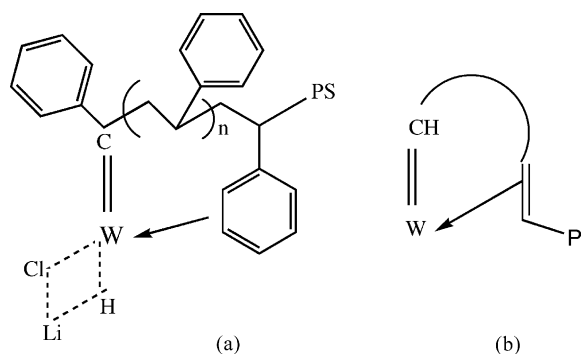
As mentioned before, in the case of PSLi and  $\text{sec-Bu-CH}_2\text{-C(Ph)}_2\text{Li}$ , high *cis*-stereoselectivities are obtained. This could be explained by means of both, the steric crowding around the metallocarbene species but also by the coordination of the metal by one aromatic double bond of the polystyryl group (Scheme 2a), which occurs in the beginning of the reaction. This is similar to the *cis*-directing species (Scheme 2b) proposed by Ivin et al. [2] favoring the *cis*-addition of monomer. The coordination of the aromatic double bond on the metal, concerning the Ziegler–Natta type catalysts, is also assumed [11].

The latter case, concerns the BuLi isomers. As it is observed the series is reversed between *sec*-Bu- and *tert*-Bu-. The same order was observed by Hsieh and Quirk [12] concerning the relative reactivities of BuLi isomers, used as initiators, in the anionic polymerization of dienes. The reactivity there was explained on the basis of degree of association of alkylolithiums. The degree of association for the *n*-BuLi is 6 and for the *sec*-BuLi and *tert*-BuLi is 4. Also aromatic solvents tends to decrease the average degree of

association, free BuLi is released, and the initiation rate was faster for the *sec*-BuLi than the *tert*-BuLi, because of the greater stability of the ion pair in the latter [12].

The same factors explain the order of BuLi concerning *cis*-stereoselectivity. The dissociation of the *sec*-BuLi takes place more easily than the corresponding *tert*-BuLi. So the initiation rate for the *sec*-BuLi/ $\text{WCl}_6$  increases relative to *tert*-BuLi/ $\text{WCl}_6$ , favoring the *cis*-selectivity. The slower formation of the active center to the system *tert*-BuLi/ $\text{WCl}_6$  facilitates the rotation of the monomer from the favoring *cis*-position to the *trans*, relative to the active center which is more stable. Finally, the *cis*-selectivity for the *n*-BuLi is normally lower than the *sec*-BuLi and *tert*-BuLi because of the higher degree of association and probably the lower steric effect on the intermediate metallocyclobutane. The degree of association explains the increase of the *cis*-selectivity when the ratio of  $\text{WCl}_6/\text{BuLi}$  increase from 1/2 to 1/4 (Table 1) because this favors the decline of the ratio of  $\text{WCl}_6/\text{BuLi}$  to the real ratio which is necessary for the formation of active center. The results for the ratio 1/4 is quite parallel to that of 1/2.

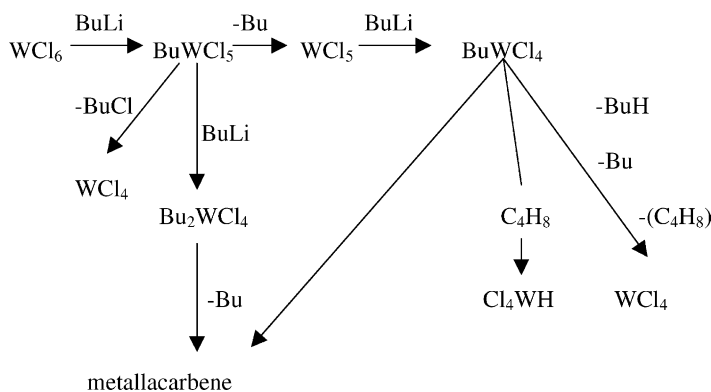
Finally, in case of  $\text{R} = \text{Me}$ , with both the co-catalysts  $\text{SnMe}_4$  and MAO the  $\sigma_c$  is 0.47 and 0.49, respectively. The  $\sigma_c$  value for the system  $\text{WCl}_6/\text{SnMe}_4$  is close to that found for the same system by Greene et al. ( $\sigma_c = 0.48$ ) [5]. These  $\sigma_c$  values were expected as result of the low bulkiness of Me group. In case of MAO as co-catalyst, which is an oligomer, it could be a steric agent but as it was supported the co-catalyst is not coordinated directly at the metal so it cannot influence the choice of the monomer entering the cage being unable to dictate the type of metallacycle formed [8]. An opposite case is that of Scheme 2a.



Scheme 2.

### 3.2. The formation of active center

The formation of the active center of the above mentioned catalytic systems follows the series shown in Scheme 3. The  $^1\text{H}$  NMR resonances during the activation of the catalytic system  $\text{WCl}_6/\text{BuLi}$ , supported the findings of other researchers [13]. The  $^1\text{H}$  NMR of *sec*-BuLi gave the resonances of the methylene and methine protons at 1.50–1.56 ppm [14]. By the addition of  $\text{WCl}_6$  broad resonances appeared at 2.1–2.3, 2.7–2.9 and 3.7 ppm which were attributed



to  $\text{Bu}_2\text{WCl}_4$ ,  $\text{BuWCl}_4$  and  $\text{BuWCl}_5$ , respectively [13d,13e]. Also the resonances appeared at 3.4 and 1.7 ppm attributed to the methine and methylene proton of *sec*-BuCl, respectively, and a peak at 5.3 ppm attributed to the methine proton of double bond of 2-butene. Analogous results were obtained with *n*-BuLi. In case of *n*-BuLi a peak obtained at 9.9 ppm attributed to the methine proton of metallacarbene. The  $^1\text{H}$  NMR results confirms the metallacarbene product of Scheme 3. Between the reaction products during the activation of catalytic system lies  $\text{WCl}_4$  (Scheme 3) and we have to take into account its stereoselectivity. According to Balcar and coworkers [15], the presence of  $\text{WCl}_4$  yield high content of *cis*-double bonds. In Table 1, the fraction of *cis*-double bonds, in the polymerization of norbornene with the catalyst  $\text{WCl}_4$  is  $\sigma_c = 0.81$ . But the catalytic activity of  $\text{WCl}_4$  is very low and slowly reaches a yield of 16% after 16 h. Since the polymerizations of norbornene with the catalytic systems  $\text{WCl}_6/\text{RLi}$  were carried out immediately the slow catalytic activity of  $\text{WCl}_4$  formed does not affect the selectivity of our catalytic systems.

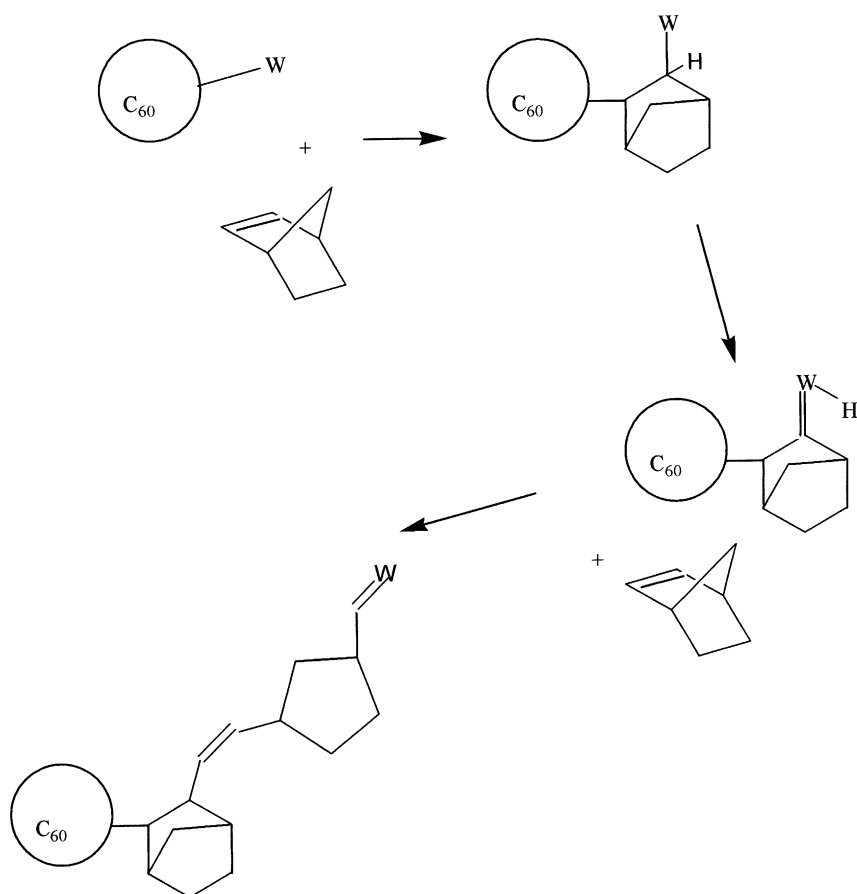
In case of the R groups *tert*-Bu, *sec*-Bu- $\text{CH}_2$ -C(Ph) $_2^-$ , *sec*-Bu $_x$ -C $_{60}^{x-}$  without an  $\alpha$ -H to form the metallocarbene, as it is concluded from  $^1\text{H}$  NMR outcomes, the first step is the insertion step, the addition polymerization of monomer on active center and then the metallocarbene is generated (Scheme 4). The ratio of  $[\text{H}_{\text{aliphatic}}]/[\text{H}_{\text{doublebond}}]$  for a pure metathesis polymerization of norbornene is 1/4, and in case of *sec*-Bu- $\text{CH}_2$ -C(Ph) $_2^-$ , *tert*-Bu and *sec*-Bu $_x$ -C $_{60}^{x-}$  is 1/4.1, 1/4.2 and 1/6, respectively.

### 3.3. Oxidation states of the W atom in ROMP catalysts based on $\text{WCl}_6$

A second factor, as mentioned above, affecting the *cis*-stereoselectivity is the oxidation state of the transition metal. Some authors assumed that the propagating species resulting from  $\text{WCl}_6$ -based catalytic systems are in the IV oxidation state ( $d^2$  electron configuration) [16] and others that they are in the V state [4,15,17]. According to the Dragutan's findings [4] the  $\text{WCl}_6$ -based catalysts, when the W atom are in a high oxidation state (V–VI) are *cis*-directing species, while when W are in the low oxidation state (III) they are *trans*-directing species. The former exhibits an octahedral configuration which has low electron density at the transition metal center ( $d^1$  and  $d^0$  electron configuration, respectively) and consequently, the electron deficiency at the orbital level ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ) imposes severe restrictions upon bond rotation and geometry relaxations. The low oxidation state (III) on the other hand exhibits a trigonal-pyramidal configuration which permits olefin rotation as a result of the relatively high electron density at the metal center ( $d^3$  configuration) and the diminished  $\pi$  character of the W–carbene bond.

In Table 2, the ESR investigation of the catalytic systems is presented. In these systems W(V) paramagnetic species are generated. The correspondence of the *g*-values of the catalytic system to the oxidation state of the metal followed the Dragutan and coworkers assignments [4,17]. They supported that the existence and the intensity of W(V) paramagnetic species





Scheme 4.

correlated fairly well with the catalyst *cis*-stereoselectivity [4]. They correlated directly the appearance of these species with the polymerization process because these species detected during the interaction of cyclopentene with the catalytic system. They also mentioned that concentration of these species, though

initially considerable, decreased dramatically during the first moments of interaction. In our case of the norbornene, being a very active monomer, metathesis polymerization process is carried out in seconds, is impossible these species during polymerization to be detected.

Table 2

The *g*-factors and formal oxidation state of catalysts derived from  $WCl_6$  and RLi compounds

Run	Catalytic system	Factor ( <i>g</i> )	Oxidation state
1	$WCl_6/sec\text{-}BuLi$ (1/1)	1.866	V
2	$WCl_6/n\text{-}BuLi$ (1/2)	1.966, 1.806	V, V
3	$WCl_6/tert\text{-}BuLi$ (1/2)	1.962, 1.806	V, V
4	$WCl_6/PSLi$ (1/2)	1.880	V
5	$WCl_6/sec\text{-}Bu\text{-}CH_2\text{-}C(Ph)_2Li$ (1/2)	1.963, 1.806	V, V
6	$WCl_6/Bu_x\text{-}C_{60}(Li)_x$ ( $x = 6$ ) (1/2)	1.960, 1.806	V, V

As it is shown in Table 2 the catalytic systems used exhibits a high oxidation state, the metal is in the W(V) state and a variety of *cis*-stereoselectivities of the poly(NBE) produced is obtained, with  $\sigma_c$  values from 0.52 to 0.96. The W(V) paramagnetic species produced seems to be consistent with metal-lacarbene formation (Scheme 3) confirmed by NMR results. Our results are in agreement to those findings which accept that the W(V) paramagnetic species are *cis*-directing species. The above mentioned data prove clearly that beyond the oxidation state of the metal, the action of R group is important for determining the stereoselectivity.

#### 3.4. The polymerization of norbornene with the catalyst $WCl_6/PSLi$

The ring-opening metathesis polymerization (ROMP) of cyclopentene with the catalytic system  $WCl_6/PSLi$  was reported by Amass and coworkers [18] and was used for the transformation reaction from anionic to metathesis to prepare block copolymers of styrene and acetylene, and in this way to synthesize soluble conducting polymers. Investigations of Thorn-Chanyi et al. [19] found that the polystyryl group of the co-catalyst is only incorporated in insignificant amount, if at all, in the high molecular weight polypentamers. Though the polymer contained only up to 0.4 mol% styrene units it still remains a very promising catalytic system for the preparation of block copolymers of acetylene [18]. However, the system  $WCl_6/PSLi$  has never been used for the polymerization of NBE.

Our interest is to investigate the ROMP of norbornene with the system  $WCl_6/PSLi$  and study the influence of polystyryl group in the *cis*-stereoselectivity of norbornene.

In Fig. 2a, the results of exclusion chromatography of polystyryl group which in turn is complexed with the  $WCl_6$  are exhibited. In Fig. 2b, the chromatogram of polymers produced with the catalyst  $WCl_6/PSLi$  is presented. Determination of molar masses are shown in Table 3.

By fractionation of the products with  $CH_3OH/CHCl_3$  (1/1) shown in Fig. 2b, the products of Fig. 2c and d were obtained. The  $^{13}C$  NMR spectrum of the product fraction of Fig. 2c exhibits its resonances at 134.27 with traces at 133.42 ppm (olefinic region), the

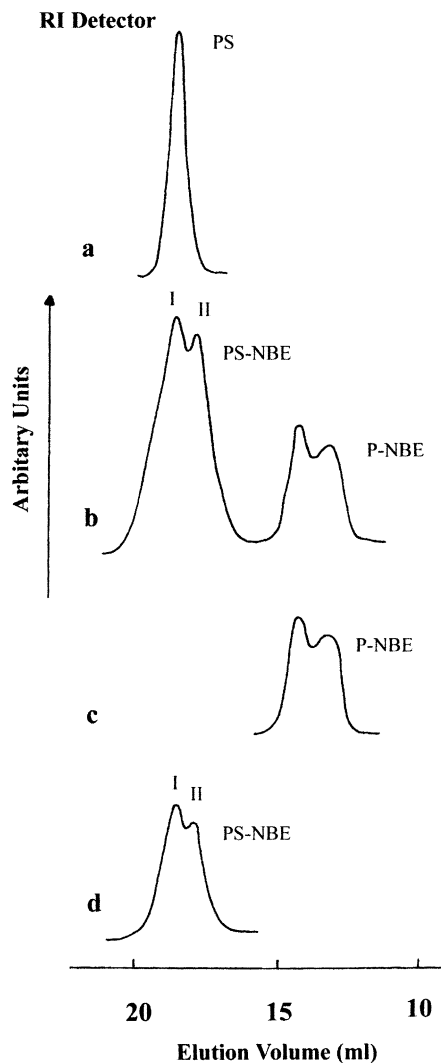


Fig. 2. GPC elution curves: (a) PSLi produced with BuLi; (b) a mixture of PS, PS-PNBE, PNBE obtained with  $WCl_6/PSLi$  catalyst. In parts c and d is shown the fractions obtained after treatment of products of chromatogram b with  $CHCl_3/CH_3OH$  (1/1); part c is attributed to PNBE and part d to PS (peak I) and PS-PNBE (peak II).

methylene resonances at 42.89 and 33.27 ppm, and the methine resonances at 38.84 ppm which confirms that an all-*cis*-poly(NBE) is produced. More informations for the microstructural features of polynorbornene produced, and the mechanism of polymerization, were obtained after the examination of the  $^{13}C$  NMR spectra of the *trans*-olefinic region (Fig. 3).



Table 3  
Determination of molar masses produced by reacting  $\text{PS}^- \text{Li}^+$  with  $\text{WCl}_6$

Polymer	Sec (RI)			D
	$M_w$	$M_n$	$M_w/M_n$	
PS	1,030	930	1.1	–
PNBE	305,400	224,000	1.36	–
PS–PNBE	6,030	4,920	1.22	3

D is the ratio  $S_1/S_2$  where  $S_1$  and  $S_2$  are the areas under the RI/Sec traces for the PS (parent) and PS–PNBE (Fig. 3d), respectively.

In Fig. 3a, the  $^{13}\text{C}$  NMR spectra of double bond region of poly(NBE) produced by  $\text{ReCl}_5$  [1] which is also a *cis*-directing catalyst ( $\sigma_c = 0.81$ ) is presented while in Fig. 3b, the corresponding olefinic region of poly(NBE) produced by  $\text{WCl}_6/\text{PSLi}$  is shown.

In catalytic systems promoting poly(NBE) with high *cis*-content there is a tendency for *trans*-double

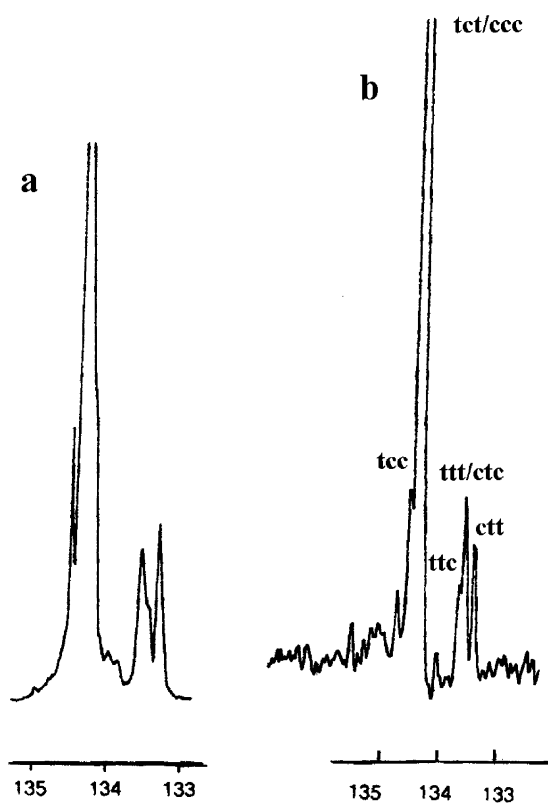
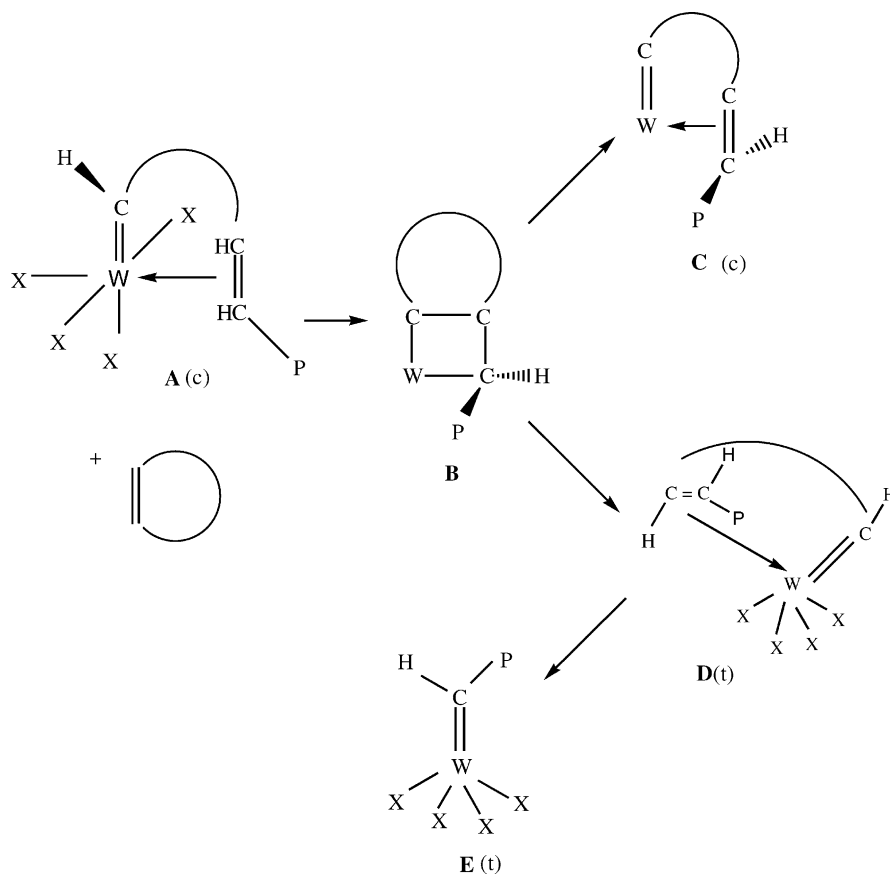


Fig. 3.  $^{13}\text{C}$  NMR spectra (double bond region) of PNBE's produced with (a)  $\text{ReCl}_5$ , 20 °C [1]; (b)  $\text{WCl}_6/\text{PSLi}$ , 20 °C.

bond to occur in pairs, i.e. *ctt* sequences tend to be preferred to *ctc*. So in  $^{13}\text{C}$  NMR spectra *trans*-olefinic carbons have a high proportion of *ttc* and *ctt* carbons relative to *ttt* and *ctc*. This was explained by Ivin and coworkers [5] with the proposed mechanism (Scheme 5), by the two main modes of metallacyclobutane **B** rupture which have been postulated to explain the stereoselectivity of reaction products. Metallacyclobutane **B** is derived from *cis*-directing metallacarbene **A(c)**. According to the first mode of rupture (Scheme 5) (conrotatory or parallel alignment of carbon double bond formed to metallacarbene) leads to the formation of chiral conformations **C(c)** of the intermediate metallacarbene, similar to **A(c)**, and seems to be characteristic of more electronegative transition metals. This rupture leads to high *cis*-polymers. The second mode of rupture (Scheme 5) (disrotatory or orthogonal alignment of carbon double bond formed to metallacarbene) leads to the formation of achiral conformations **D(t)**, **E(t)** of the intermediate metallacarbene which are *trans*-directing and seems to prevail for less electronegative metals.

In our case (Fig. 3b) it is shown that *ttt/ctc* line is not smaller but it is approximately of the same intensity with *ttc/ctt* lines. To explain this we make the assumption that, in the beginning steps of the reaction, the bulkiness of polystyryl group and the coordination of double bond of phenyl group on the metal (Scheme 2a) inhibits the formation of **D(t)**, at least in the extension of the corresponding case of Scheme 5. Moreover, the existence of three peaks *ttc*, *ttt/ctc*, *ctt* indicate that the microstructure of poly(NBE) is *cis*-syndiotactic [2,8] proving the stereocontrol of the reaction.

In chromatogram, Fig. 2d, peak I is attributed to the initial polystyrene produced (PSLi) and then complexed to  $\text{WCl}_6$ . The  $^{13}\text{C}$  NMR spectrum of the product of Fig. 2d, consist of three major absorptions, 147.2, 146.8 and 146.3 ppm, which were assigned to the *mm*, *mr* and *rr* triads of the aromatic  $\text{C}_1$  carbon of polystyrene [20]. The  $^{13}\text{C}$  NMR spectrum also exhibits an absorption at 133.88 ppm attributed to *cis*-poly(NBE). In addition broadening of the peak is observed in the methine and methylene region (40.9 and 43.2 ppm, respectively) indicating that the polymer is not a mixture of polystyrene and poly(NBE) but a copolymer between them. The content of NBE



Scheme 5.

unit in the copolymer was calculated from the  $^{13}\text{C}$  NMR spectrum, comparing the aromatic and olefinic region of polystyrene and poly(NBE), respectively, and taking into account the ratio  $D$  (Table 3), estimated to be 7%.

Finally, the resultant molecular mass distribution is the familiar bimodal one referred to poly(NBE)'s produced with  $\text{WCl}_6$ -based catalytic systems [21]. This does not indicate that there are two different catalytically active species but the oligomer/polymer ratio controlled by a ring chain equilibrium. The narrow molar mass distribution of 1.36 for poly(NBE) and the shape of chromatogram indicate that the very fast reaction favors the competition between the propagation and the intramolecular reaction in equilibrium amounts of polymer and oligomer of standard composition excluding a large series of various oligomers.

#### 4. Conclusion

In the polymerization of norbornene with the catalysts  $\text{WCl}_6/\text{RLi}$ , the bulkiness of R chain and the coordination of side substituents of R chain on the metal proved determining factors of *cis*-stereoselectivity. Although, with all the catalytic systems used, a  $\text{W(V)}$  paramagnetic species is produced leading to *cis*-poly(NBE), the variety of the *cis*-stereoselectivities obtained depend on the above mentioned two factors. This is confirmed in the case of the catalytic system  $\text{WCl}_6/\text{PSLi}$  which leads to an all-*cis*-poly(NBE) and in the case of  $\text{WCl}_6/\text{sec-Bu-CH}_2\text{-C(Ph)}_2\text{Li}$  which leads to a high *cis*-content poly(NBE). Less bulky groups as the Bu and the Me groups leads to poly(NBE) with less *cis*-content, respectively. Contrary, in the case of  $\text{WCl}_6/\text{sec-Bu}_x\text{-C}_{60}(\text{Li})_x$  ( $x = 6$ ), although a

bulky group appears, the *cis*-content of poly(NBE) obtained, is not similar to that of  $\text{WCl}_6/\text{PSLi}$  and  $\text{WCl}_6/\text{sec-Bu-CH}_2\text{-C(Ph)}_2\text{Li}$ . This was attributed to two factors: the first being the very strong crowding surround the metal which does not permit the easy access of the monomer to the metal because of the star architectures formed (Scheme 1). The second is the destroyed conjugated structure of  $\text{C}_{60}$  which does not permit the formation of intermediate of Scheme 2a.

Finally, steric factors of *cis*-stereoselectivity also explain why, the high *cis*-content poly(NBEs) produced with the catalytic systems used, does not give the tendency to the central *trans*-peak of the olefinic region to diminish. This last point is confirmed by  $^{13}\text{C}$  NMR (Fig. 3b).

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