# RING OPENING METATHESIS POLYMERIZATION OF NORBORNENE BY $WCl_6$: FORMATION OF $WCl_5$ AND $WCl_4$ AND THEIR CATALYTIC ACTIVITY

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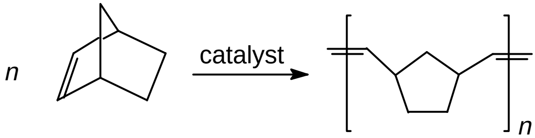
*Dedicated to Professor Jaroslav Podlaha on the occasion of his 60th birthday.*

Reaction between $WCl_6$ and norbornene in benzene and cyclohexane, respectively, was investigated using UV/VIS, ESR and XPS spectroscopy in order to establish the main reaction products on the tungsten side and their relation to the initiation of ring opening metathesis polymerization (ROMP) of norbornene. The tungsten compounds: $WCl_5$, insoluble $WCl_4$ and soluble tungsten species having four chlorine atoms bound to tungsten, $[WCl_4L_n]$ were found to be the main products. The catalytic activity of the respective compounds in ROMP of norbornene was found to decrease in the order: $WCl_5 > WCl_6 >> WCl_4 \approx [WCl_4L_n]$. The polynorbornenes prepared with both $WCl_4$ and $[WCl_4L_n]$ possess higher content of *cis* double bonds in comparison with polymers prepared with $WCl_6$ and $WCl_5$ catalysts.

**Key words:** Ring opening metathesis polymerization; Norbornene; Tungsten chlorides.

Ring opening metathesis polymerization (ROMP) of norbornene (NBE) (Eq. *1*) and its derivatives (e.g. dicyclopentadiene – DCPD) belongs to the reactions of theoretical and practical importance.



(*1*)

A large number of the catalyst systems practically used are based on $WCl_6$ and/or $WOCl_4$ in combination with a reducing cocatalyst. In addition, it was found that both these chlorides exhibit moderate activity in ROMP of NBE-type hydrocarbons even without any cocatalyst[1–3], probably due to their quick reduction by the substrates followed by formation of catalytically active tungsten carbene complexes[4].

The reduction of $WCl_6$ by alkenes and cycloalkenes was studied by several authors[5–8]. Numerous organic products (chlorinated hydrocarbons, oligomers) were identified indicating the complex nature of this reaction. However, little reliable information concerning the products on the tungsten side is available. On the basis of presence of 1,2-dichloronorbornane in the reaction products, Laverty and Rooney[6] have suggested that NBE reduces $WCl_6$ to $WCl_4$ and that the last substance can be considered a precursor of the active species for oligomerization and ROMP of NBE. On the other hand, Thorn-Csányi et al. investigated the reaction of $WCl_6$ with both cyclopentene and norbornene by UV/VIS spectroscopy[7,8] and found that $WCl_6$ was nearly quantitatively converted to $WCl_5$.

Studying the catalytic activity of $WCl_6$ as a unicomponent catalyst in polymerization of NBE and DCPD, we observed[3] formation of substantial amounts of a dark brown precipitate of unknown composition immediately after mixing $WCl_6$ with the substrate. Therefore, we considered worthwhile to reinvestigate the stoichiometric reaction of $WCl_6$ with NBE under conditions close to those used in catalytic experiments to detect the main products on the tungsten side and to find their relation to ROMP initiation.

## EXPERIMENTAL

### Chemicals

$WCl_6$ (Fluka, 90–95% purity) was purified by sublimation in vacuo and its purity was tested by UV/VIS spectroscopy (in benzene); $WCl_5$ was prepared by the reduction of $WCl_6$ with red phosphorus[9] and sublimed in vacuo; $WCl_4$ (Aldrich, 97% purity) was used without any purification; NBE (Fluka, purum) was distilled from NaH; benzene was purified with $H_2SO_4$, refluxed in vacuo over NaH and degassed – details are given elsewhere[10].

### Procedures and Methods

All operations were carried out in vacuum all-glass apparatuses (for details see ref.[10]). The polymers were isolated using methanol (containing approximately 0.1 wt.% of 2,5-di-*tert*-butylhydroquinone as antioxidant) and dried in vacuo at 40 °C. The UV/VIS spectra were recorded on a Hewlett–Packard HP 89 500 spectrometer using evacuated cells ($l$ = 0.1 cm).

The electron spin resonance (ESR) spectra were recorded on an ESR-200 spectrometer (ZWG, Berlin). The IR spectra of polymers were measured on a Specord 75 IR spectrometer in KBr pellets.

The XPS measurements were conducted on a VG ESCA 3 Mk II electron spectrometer. The background pressure was ≈ $10^{-6}$ Pa. The measurements were performed using $AlK_\alpha$ ($h\nu$ = 1 486.6 eV) radiation. The spectrometer was operated with a pass energy of 20 eV giving the resolution of 1.1 eV on $Au(4f_{7/2})$ line. The spectra were calibrated using C(1s) binding energy of carbon (1s) electrons at 285.0 eV. The specimens were prepared by spreading the powder samples on double sided adhesive tape attached to the specimen probe. Samples were loaded into the spectrometer in pure nitrogen using a glove box attached to the preparation chamber of the spectrometer. Spectra of W(4f) and Cl(2p) electrons were recorded. The curve fitting of the high resolution spectra was accomplished using the lines of Gaussian–Lorentzian shape[11]. The core level binding energies were determined with an accuracy of $\mp 0.2$ eV. The peak area computation was performed after the non-linear background was removed[12]. The quantification of the chlorine/tungsten ratio was accomplished by correcting the photoelectron peak areas for their cross sections[13].

The X-ray diffraction studies were carried out using $CuK_{\alpha_{1,2}}$ radiation. The sample was placed under dry argon into the glass capillary tube (diameter of 0.7 mm) the ends of which were closed to avoid interaction of the sample with atmosphere.

## RESULTS AND DISCUSSION

### *The Tungsten Products Formed in the Reaction of $WCl_6$ with Cocatalytic Amount of NBE*

If a concentrated solution of $WCl_6$ in benzene or cyclohexane (initial concentration $[WCl_6]_0$ = 0.01 mol/l) is mixed with NBE (molar ratio NBE/$WCl_6$ = 3) at room temperature a dark brown, rapidly sedimenting precipitate appears in the reaction mixture. The UV/VIS spectra of the supernatants were recorded in the course of the reactions. After 14 days, when no further changes in UV/VIS spectra were observed, the precipitates were isolated, washed with benzene or cyclohexane, respectively, and dried by lyophilization (all the operations were carried out in vacuum). The precipitates were found to be unstable in air (therefore, they were further handled under argon) and insoluble in nonpolar organic solvents such as benzene, cyclohexane or chloroform. X-Ray photoelectron spectroscopy (XPS) was applied for the analysis. The same atomic ratio Cl/W = 4.0 ∓ 0.1, corresponding to the stoichiometry $WCl_4$, was found by the XPS analysis for all the precipitates, whatever solvent having been used in the $WCl_6$ + NBE reaction. The measured value of the binding energy of $W(4f_{7/2})$ electrons, 35.2 eV, is consistent[14] with the found composition. Bands of oxygen and carbon were also found in the photoelectron spectra of both samples. The band of oxygen was weak and almost disappeared after 2 min of etching by argon ions with an energy of ≈2 keV. This result indicated that oxygen was probably present as a surface contamination. The C(1s) line remains in the spectrum after ion etching, and it probably results from the residues of solvent and/or some reaction products in the sample.

The X-ray diffraction profile of the sample was dominated by the lines corresponding[15] to $WCl_4$ which were broadened due to the small mean size of the precipitate particles. The yield of $WCl_4$ precipitated in the reaction of $WCl_6$ with NBE under the above-given condition was approximately 55% regardless of solvent.

The UV/VIS spectra of the supernatants at the final stage of the reaction between $WCl_6$ and NBE in benzene and cyclohexane are shown in Fig. 1. In the case of the benzene solution, the resulting spectrum displays three main bands with maxima at 300 nm, 348 nm and in the region from 464 nm to 482 nm. A comparison of the band intensities for various concentrations of reactants and reaction times suggests that the maxima correspond to three different species. The band at 348 nm was assigned to $WCl_5$ on the basis of comparison with the spectrum of an authentic sample of $WCl_5$. The presence of

$WCl_5$ in the reaction mixture studied was also confirmed by ESR after addition of methyl palmitate in slight excess (signal at $g = 1.769$ appeared, which was described earlier in the course of the reaction between $WCl_5$ and methyl palmitate[16]). For the reaction of $WCl_6$ with NBE in cyclohexane, the band of $WCl_5$ (at 360 nm) was also observed, but it disappeared slowly with concomitant increase of the band at 310 nm. The fact that $WCl_5$ remained unreacted among reaction products in benzene is probably due to a consumption of NBE in benzene alkylation and/or NBE oligomerization. Considerable amounts of phenylnorbornane (one isomer – probably 2-phenylnorbornane), diphenylnorbornane (three isomers) and several kinds of NBE dimers bearing one or two phenyl groups were actually found (by GC/MS) in the reaction mixture prepared in benzene in accord with the findings of Rooney et al.[2].

The product exhibiting maximum absorption at 310 nm in cyclohexane was isolated from the supernatant after the reaction $WCl_6$ + NBE in cyclohexane ($[WCl_6]_0 = 0.01$ mol/l, molar ratio $NBE/WCl_6 = 3$, room temperature, 14 days of reaction). After stripping the solvent in vacuo, a yellow waxy solid was obtained which was unstable in air and very well soluble in benzene or cyclohexane. The overall stoichiometry of this material as obtained by XPS analysis was $WCl_6C_{240}$. The shape and width of the Cl(2p) spectrum indicate the presence of two chemical states of chlorine. By fitting the spectrum we obtained the difference between the $Cl(2p_{3/2})$ components equal to 1.2 eV, and the composition of the product may be rewritten as $WCl^{\alpha}_4Cl^{\beta}_2C_{240}$. The $Cl^{\alpha}$ chemical state is assignable to chlorine atoms linked to W atoms, while $Cl^{\beta}$ are probably linked to some organic moiety. The measured value of $W(4f_{7/2})$ core level binding energy (35.4 eV) is consistent[14] with this assignment. The C(1) signal is dominated by the contribution coming from the reaction products (e.g. chloronorbornanes, NBE oligomers) present in the sample. Consequently, the XPS method allowed neither to discriminate between carbon atoms coordinated to W and those present in the organic reaction products nor to determine the composition of the organic ligand (or ligands) linked to W atom. The

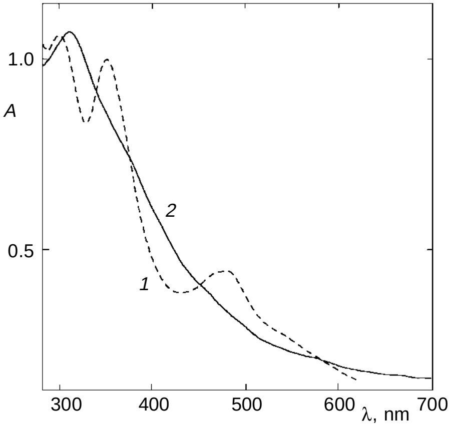


FIG. 1
UV/VIS spectra of the supernatants of $WCl_6$/NBE (1 : 3) mixtures after 14 days of reaction: *1* in benzene, *2* in cyclohexane; $[WCl_6]_0$ = 10 mmol/l, room temperature

presence of these ligands may be responsible for the solubility of the sample, which is henceforth denoted as $[WCl_4L_n]$.

We have not yet succeeded, however, in isolation and identification of compounds corresponding to the bands which appeared in benzene in the region 464–480 nm. These bands, however, were not observed in the spectrum if a high excess of NBE was added to the $WCl_6$ solution (vide infra).

### *Catalytic Experiments*

If a great excess of NBE is added to a saturated benzene solution of $WCl_6$ (resulting $[WCl_6]_0$ = 17 mmol/l, molar ratio NBE/$WCl_6$ = 100, room temperature), a formation of the $WCl_4$ precipitate is visible immediately after mixing. The amount of $WCl_4$ formed, as determined by gravimetry after hydrolysis and transformation into $WO_3$, represents 54% of the starting amount of $WCl_6$. In the UV/VIS spectrum of the supernatant recorded 60 s after mixing the reactants, the band of $WCl_5$ was observed with intensity corresponding to a $WCl_5$ concentration about 4.5 mmol/l accompanied only with the band at 300 nm. The $WCl_5$ band disappeared completely within the next 30 min but the maximum at 300 nm persisted. On the other hand, in diluted benzene solutions of $WCl_6$ ($[WCl_6]_0$ = 2 mmol/l) no formation of the precipitate was observed in the reaction of $WCl_6$ with a great excess of NBE (molar ratio NBE/$WCl_6$ = 100–420). The UV/VIS spectra showed that almost all $WCl_6$ was transformed into $WCl_5$, which then slowly reacted and gave the product(s) with absorption at 300–310 nm. The difference in behaviour of concentrated and diluted solution of $WCl_6$ need not result from the reaction kinetics only. Concentrated solutions of $WCl_6$ are most probably colloidal which may facilitate the formation of $WCl_4$ precipitate.

The data concerning the results of the experiments in which ROMP of NBE was initiated by $WCl_x$ compounds ($x$ = 6, 5, 4) under various conditions are summarized in Table I. The catalytic activity is expressed in terms of the polymer yield achieved in a given reaction time $t$. The polymers prepared were characterized using IR spectroscopy. In the infrared spectra of the polymers there are three strong bands in the region below 1 600 $cm^{-1}$: at 740 $cm^{-1}$ $\delta(H–C=)_{cis}$ , at 966 $cm^{-1}$ $\delta(H–C=)_{trans}$ and at 1 440 $cm^{-1}$ $\delta(CH_2)$. The presence of the band at 966 $cm^{-1}$ clearly demonstrates that ROMP of NBE occurred. The ratios of absorbance at 966 $cm^{-1}$ and 740 $cm^{-1}$ ($A_{966}/A_{740}$) characterizing the polymer configurational structure are given in Table I.

In experiment No. 1, concentrated solution of $WCl_6$ in benzene was used as a catalyst. The catalytic activity of a suspension of $WCl_4$ in benzene was tested in the experiments Nos 2–5.

$WCl_4$(A) is the sample isolated from the products of the reaction of $WCl_6$ with NBE (under the conditions given above), $WCl_4$(B) is the sample of a commercial product. Both samples exhibited significant activity for ROMP of NBE. Especially considerable polymer yields were achieved when using high monomer concentrations. However, the content of *cis* double bonds of the polymers is significantly lower than that of the polymer prepared in experiment No. 1. No dissolution of $WCl_4$ was observed either before addition of the monomer or during the polymerization. The UV/VIS spectrum of the liquid phase after addition of benzene to $WCl_4$ did not show any distinct bands at $\lambda > 290$ nm and, during the polymerization, the benzene phase was colourless. In this connection it should be mentioned that insoluble $WCl_4$ as well as another insoluble W(IV) compound formulated as $WOCl_2$ have recently been found to be active in a similar process – phenylacetylene polymerization[17,18].

In experiment No. 6, a benzene solution of $[WCl_4L_n]$ (isolated from the products of the reaction of $WCl_6$ with a stoichiometric amount of NBE in cyclohexane as given above) was used as a catalyst. Its concentration of 8 mmol/l represents roughly the

TABLE I
Polymerization of norbornene (NBE) with tungsten chlorides: polymer yields (*Y*) and the ratios of IR absorbancies at 966 $cm^{-1}$ and 740 $cm^{-1}$ ($A_{966}/A_{740}$) of the polymers prepared. $c_0$(NBE) = initial NBE concentration in mol $dm^{-3}$, *R* = molar ratio monomer/catalyst, *T* = reaction temperature, *t* = reaction time

| No. | Catalyst | $c_0$(NBE) mol $dm^{-3}$ | *R* | *T*, °C | *t*, h | *Y*, % | $A_{966}/A_{740}$ |
|---|---|---|---|---|---|---|---|
| 1 | $WCl_6$ | 1.7 | 100 | 25 | 1.5 | 4 | 2.95 |
| | | | | | 22 | 58 | 2.40 |
| 2 | $WCl_4$(B) | 1.7 | 100 | 25 | 1.5 | 0.5 | – |
| | | | | | 22 | 18 | 1.20 |
| 3 | $WCl_4$(A) | 2.7 | 100 | 25 | 1 | 14 | 1.73 |
| 4 | $WCl_4$(B) | 2.7 | 100 | 25 | 19 | 25 | 1.78 |
| 5 | $WCl_4$(B) | 4.5 | 100 | 25 | 19 | 70 | 1.41 |
| 6 | $[WCl_4L_n]$ | 1.7 | 213 | 25 | 1.5 | 3.5 | 1.72 |
| | | | | | 22 | 31 | 1.10 |
| 7 | $WCl_6$ | 0.84 | 420 | 50 | 1 | 14 | 2.71 |
| | | | | | 3 | 62 | 2.56 |
| | | | | | 9 | 95 | 2.38 |
| 8 | $WCl_5$ | 0.84 | 420 | 50 | 1 | 48 | 2.62 |
| | | | | | 3 | 79 | 2.71 |
| | | | | | 9 | 98 | 2.63 |
| 9 | $[WCl_4L_n]$ | 0.84 | 420 | 50 | 1 | 0.6 | – |
| | | | | | 3 | 2.8 | – |
| | | | | | 9 | 2.0 | – |
| 10 | $WCl_4$(B) | 0.84 | 420 | 50 | 3 | 0.4 | – |

$WCl_4$(A) sample prepared by the reaction of $WCl_6$ with NBE, $WCl_4$(B) sample of commercial product.

concentration of soluble tungsten compounds in experiment No. 1 (conversion of $WCl_6$ into insoluble $WCl_4$ = 54%, see above). Although $[WCl_4L_n]$ exhibits significant catalytic activity, it provided a polymer with the content of *cis* double bonds similar to that of polymers prepared with solid $WCl_4$ and therefore lower in comparison with the polymer from experiment No. 1. This difference in polymer configurational structure suggests that in the polymerization initiated by $WCl_6$, the reaction takes place predominantly on catalytic centres differing from those formed from $[WCl_4L_n]$ and/or solid $WCl_4$.

Experiments Nos 7–9 compare the catalytic activity of $WCl_6$, $WCl_5$ and $[WCl_4L_n]$ under conditions where no insoluble $WCl_4$ is formed. For comparison, a polymerization experiment with solid $WCl_4$ (No. 10) was conducted under the same conditions. To obtain reasonable polymer yields within the intervals of several hours, elevated reaction temperature and molar ratio NBE/W = 420 were used. Under these conditions, both $[WCl_4L_n]$ and $WCl_4$ solid, exhibited nearly negligible activity in comparison with $WCl_6$ and $WCl_5$. In addition to this, the polymers prepared with $WCl_5$ had a *cis*/*trans* ratio similar to that of the polymers prepared using $WCl_6$. It can be just concluded that from all tungsten species detected as products of the $WCl_6$ reduction by NBE, only $WCl_5$ can be regarded as a main precursor of catalytic centres for the NBE polymerization initiated by $WCl_6$.

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