

## Ring-opening metathesis polymerization of dicyclopentadiene by unicomponent catalysts derived from $WCl_6$

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### Abstract

The complexes  $WCl_5(OR)$ , where  $R = -CH-(CH_2Cl)_2$  or substituted phenyl, and  $WOCl_4$  have been found to initiate ring-opening metathesis polymerization of dicyclopentadiene without any co-catalyst. Their activities are, however, lower than when they are associated with a reducing organometallic co-catalyst. The unicomponent catalysts afford a slightly crosslinked, partially soluble polymer with a relatively high content of *cis* double bonds in the main chain.

### Introduction

Dicyclopentadiene (DCPD) is one of the cheapest and most active monomers for ring-opening metathesis polymerization (ROMP). It can be polymerized by a variety of catalytic systems [1]. The most widely used systems consist of a combination of transition metal compounds (*e.g.*,  $WCl_6$ ) and organometallic co-catalysts. To enhance solubility and activity,  $WCl_6$  has been modified by addition of phenols or other oxygen-containing compounds [2]. It has also been reported [3, 4] that DCPD as well as other norbornene derivatives undergo ROMP by  $WCl_6$  alone. In this paper, we want to show how oxygen-containing ligands on tungsten influence the catalytic activity and selectivity in DCPD polymerization by unicomponent catalysts derived from  $WCl_6$ . For this purpose, the complexes  $WCl_{6-x}(OR)_x$ , where  $x = 1, 2$  and  $R = -CH-(CH_2Cl)_2$  or substituted phenyl, were prepared and tested in polymerization experiments.

Phenoxo- and alkoxochlorides of tungsten have been described as efficient metathesis catalysts only in combination with organometallic co-catalyst [5, 6]. Recently, aryloxo complexes  $WCl_{6-x}(OAr)_x$  (where  $x = 2, 3, 4$ ) have been applied as catalysts for DCPD ring-opening metathesis polymerization when associated with alkyl-aluminium, alkyl-tin or alkyl-lead compounds [7].

## Experimental

### Chemicals

$\text{WCl}_6$  and  $\text{WOCl}_4$  were purified by sublimation *in vacuo*, and their purity was checked by UV-Vis spectroscopy. Epichlorohydrin and phenols (commercial products, p.a.) were used without special purification. DCPD (provided by Chemical Plants Litvinov, C.S.F.R.) was stripped with nitrogen, had traces of peroxides removed using neutral alumina, and was finally degassed *in vacuo*.

### Procedures

All procedures were carried out *in vacuo*, in all-glass apparatus. The reaction components were charged into the reaction vessel using breakable seals. The UV-Vis spectra were recorded on a Hewlett-Packard HP 89500 spectrometer with the samples in sealed, evacuated cuvettes. The IR spectra were recorded on a Specord 75 IR instrument using KBr cuvettes or KBr pellets.

### Catalyst preparation

$\text{WCl}_{6-x}(\text{OR})_x$  complexes were prepared by reaction of  $\text{WCl}_6$  with epichlorohydrin (ECH) or the following substituted phenols: 2,6-di-*t*-butylphenol, 4-*t*-butylphenol and 4-chlorophenol. Benzene solutions of  $\text{WCl}_6$  and epichlorohydrin or phenol were mixed together at lab temperature in an ampoule equipped with a cuvette. The course of the reaction was followed by UV-Vis spectroscopy. In the cases of 4-*t*-butylphenol and 4-chlorophenol, the reaction mixture was heated until all  $\text{WCl}_6$  disappeared. Complexes derived from ECH were used without isolation.  $\text{WCl}_5(\text{OAr})$  complexes were isolated (by removing benzene *in vacuo*) as dark violet solid products, unstable in air. The product of the reaction of  $\text{WCl}_6$  with 4-*t*-butylphenol at a molar ratio of 1:2 was isolated in a similar way as a dark brown solid; as shown by UV-Vis spectroscopy, it did not contain any  $\text{WCl}_6$  but it could contain some amount of  $\text{WCl}_5(\text{O}-4\text{-t-Bu-C}_6\text{H}_4)$ .

### Polymerization procedure

DCPD was added to the solution of catalyst under mixing and at lab temperature. Then the reactor was placed into thermostatted water. The reaction stopped upon addition of methanol. The polymer was precipitated in methanol containing 2,5-di-*t*-butyl-hydroquinone as antioxidant. The soluble polymer part was separated by dissolving the sample in benzene at lab temperature for 24 h.

## Results

The product of the reaction of  $\text{WCl}_6$  with ECH at a molar ratio of 1:1 is characterized by an absorption band at  $\lambda = 350$  nm; if ECH is used in

twofold excess this band appears transiently and the final spectrum shows only a continual decrease of absorbance above  $\lambda=290$  nm (Fig. 1). The formation of  $\text{WCl}_{6-x}[\text{OCH}(\text{CH}_2\text{Cl})_2]_x$  (where  $x=1, 2$ ) is assumed according to the literature [5].

The UV-Vis spectra of  $\text{WCl}_5(\text{OAr})$  complexes are given in Fig. 2. At room temperature, 2,6-di-*t*-butylphenol and  $\text{WCl}_6$  (at a molar ratio of 1:1) react relatively slowly and quantitatively. In the cases of both 4-*t*-butylphenol and 4-chlorophenol, substitution to the second degree proceeds more rapidly than to the first degree and therefore the final mixtures contain certain amounts of  $\text{WCl}_{6-x}(\text{OAr})_x$  ( $x>1$ ) and unreacted  $\text{WCl}_6$ . This is in accordance with the results of Quignard *et al.* [8], who prepared various  $\text{WCl}_{6-x}(\text{OAr})_x$  complexes for  $x\geq 2$  but did not succeed for  $x=1$ . Under our conditions, however, the bands corresponding to  $\text{WCl}_6$  and multiply substituted chlorides disappear after heating and the final spectra resemble that observed in the case of 2,6-di-*t*-butylphenol product. The IR spectra of the complexes prepared (benzene solution, 400–1250  $\text{cm}^{-1}$  region) are characterized by the following bands:  $\text{WCl}_5(\text{O}-4\text{-Cl-C}_6\text{H}_4)$ : 515 (w), 717 (m), 827 (s), 911 (m), 1003 (w), 1087 (s), 1140 (w), 1223 (m)  $\text{cm}^{-1}$ ;  $\text{WCl}_5(\text{O}-4\text{-t-Bu-C}_6\text{H}_4)$ : 753 (m), 766 (w), 840 (s), 917 (m), 1010 (w), 1113 (m), 1147 (w), 1230 (m)  $\text{cm}^{-1}$ ;  $\text{WCl}_5(\text{O}-2,6\text{-di-t-Bu-C}_6\text{H}_3)$ : 453 (m), 547 (m), 573 (w), 757 (s), 820 (w), 833 (w), 907 (m), 1010 (w), 1083 (m), 1117 (s), 1203 (w)  $\text{cm}^{-1}$ .

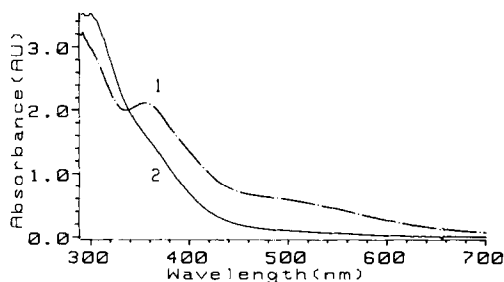


Fig. 1. UV-Vis spectrum of the product of the reaction of  $\text{WCl}_6 + \text{ECH}$  at molar ratios of 1:1 (curve (1)) and 1:2 (curve (2)) in benzene.

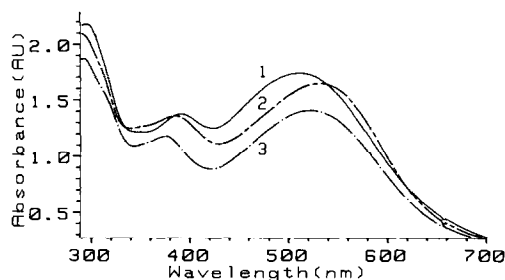


Fig. 2. UV-Vis spectra of the complexes  $\text{WCl}_5(\text{OAr})$  in benzene: (1)  $\text{Ar}=4\text{-Cl-C}_6\text{H}_4$ ,  $c=1.4$   $\text{mmol l}^{-1}$ ; (2)  $\text{Ar}=4\text{-t-Bu-C}_6\text{H}_4$ ,  $c=1.4$   $\text{mmol l}^{-1}$ ; (3)  $\text{Ar}=2,6\text{-di-t-Bu-C}_6\text{H}_3$ ,  $c=1$   $\text{mmol l}^{-1}$ .  $l=0.1$  cm.

Results of polymerization experiments are summarized in Table 1. Catalytic activity is characterized by the polymer yield after a given time. The DCPD conversion determined by GC was in some cases about several percent higher than the polymer yield, suggesting formation of a methanol-soluble low-molecular-weight product.  $WCl_6$  after addition of DCPD provides a black precipitate, which partially redissolves at later stages. The inhomogeneity of the reaction mixture leads, however, to decreased reproducibility of results. Other catalysts listed in Table 1 provide homogeneous systems, and their activity at room temperature increases with R in the following series: 2,6-di-t-Bu-C<sub>6</sub>H<sub>3</sub> < 4-t-Bu-C<sub>6</sub>H<sub>4</sub> <  $WCl_6$  < 4-Cl-C<sub>6</sub>H<sub>4</sub> <  $WOCl_4$  <  $CH(CH_2Cl)_2$ . In all cases, a strong increase in activity occurs with increasing temperature. Modification of  $WCl_6$  by a twofold excess of phenol or ECH leads to a strong drop in catalytic activity.

Polymer products were separated into benzene-soluble and benzene-insoluble fractions. The amount of soluble fraction depended on DCPD conversion. At low conversion, soluble polymer was formed predominantly, but at high conversion, crosslinked polymer strongly prevailed (Fig. 3). This suggests that in the initial stage linear polymer is formed according to eqn. (1), and is later crosslinked by opening of the cyclopentene rings.

TABLE 1

Polymerization of DCPD by unicomponent catalysts derived from  $WCl_6$

| No. | Catalyst                      | Temp.<br>(°C) | Time<br>(h) | Yield<br>(%) | Sol.<br>fr.<br>(%) | IR characterization<br>( $A_{973}/A_{755}/A_{1445}$ ) |                 |
|-----|-------------------------------|---------------|-------------|--------------|--------------------|---|-----------------|
|     |                               |               |             |              |                    | Soluble fraction                                      | Insol. fraction |
| 1   | $WCl_6$                       | lab           | 24          | 25           | 40                 | 0.72/1.45/1   | —               |
| 2   |                               | 70            | 1           | 66           | 10                 | —   | 0.86/1.43/1     |
| 3   | $WCl_5[O-CH-(CH_2Cl)_2]$      | lab           | 3           | 59           | 0                  | —   | 0.81/1.51/1     |
| 4   | $WCl_4[O-CH-(CH_2Cl)_2]_2$    | lab           | 24          | 0            | —                  | —   | —               |
| 5   | $WCl_5(O-2,6-di-t-Bu-C_6H_3)$ | lab           | 24          | 3            | 100                | 1.38/0.89/1   | —               |
| 6   |                               | 70            | 6           | 20           | 10                 | —   | 1.19/1.13/1     |
| 7   | $WCl_5(O-4-t-Bu-C_6H_4)$      | lab           | 24          | 6            | 80                 | 0.48/0.80/1   | —               |
| 8   |                               | lab           | 50          | 24           | 58                 | —   | —               |
| 9   |                               | 70            | 2           | 51           | 9                  | 0.68/1.16/1   | 0.84/1.30/1     |
| 10  | $WCl_5(O-4-Cl-C_6H_4)$        | lab           | 24          | 29           | 33                 | 0.24/0.53/1   | 0.72/1.41/1     |
| 11  |                               | 40            | 6           | 23           | 17                 | 0.25/0.88/1   | 0.82/1.17/1     |
| 12  |                               | 70            | 2           | 46           | 9                  | 0.48/0.94/1   | 0.74/0.98/1     |
| 13  | $WCl_4(O-4-t-Bu-C_6H_4)_2$    | 70            | 6           | 7            | 73                 | 0.88/1.48/1   | —               |
| 14  | $WOCl_4^a$                    | lab           | 3           | 21           | 20                 | —   | —               |
| 15  |                               | 70            | 1           | 67           | 3                  | 0.88/0.79/1   | 1.29/0.95/1     |

Conditions: benzene;  $[W^0] = 20 \text{ mmol l}^{-1}$ ; molar ratio DCPD/catalyst = 74/1.

<sup>a</sup> $[W^0] = 10 \text{ mmol l}^{-1}$ .

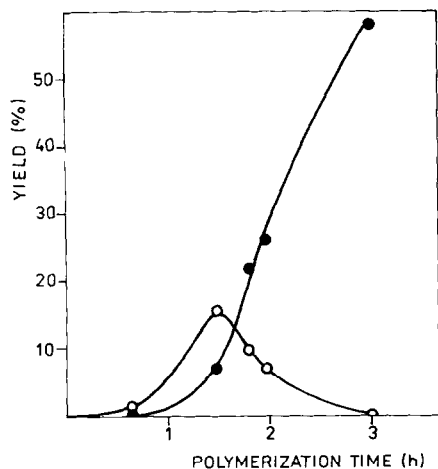
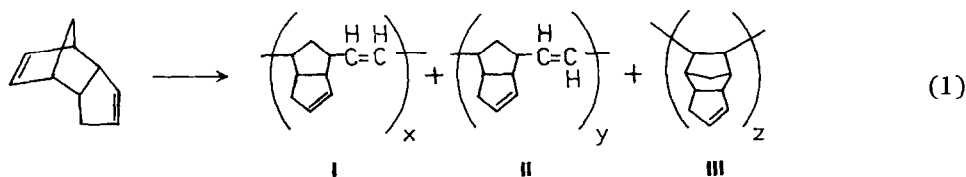


Fig. 3. The course of DCPD polymerization initiated by  $\text{WCl}_5(\text{O}-\text{CH}(\text{CH}_2\text{Cl})_2)$ : (○) soluble polymer fraction; (●) insoluble polymer fraction. Lab temperature; molar ratio DCPD/catalyst = 74/1.



The polymer structure was studied by IR spectroscopy. The presence of bands corresponding to the double bonds along the main chain ( $973$ ,  $755$ ,  $1408$  and  $3000 \text{ cm}^{-1}$ ) confirms that ROMP took place. The presence of the cyclopentene-ring double-bond band at  $1620 \text{ cm}^{-1}$  and the absence of the band corresponding to the double-bond vibration in a norbornene ring at  $1575 \text{ cm}^{-1}$  suggest that ROMP proceeds predominantly by opening of the norbornene ring, giving rise to structures **I** and **II** in eqn. (1). In addition, the polymer can contain a certain amount of structure **III** as a result of the catalyst acidity. For estimating the **II/I** ratio, the values of the absorbances at  $973 \text{ cm}^{-1}$  and at  $755 \text{ cm}^{-1}$  (C–H def. vibr. in *trans* and *cis* double bond, respectively) relative to the absorbance at  $1445 \text{ cm}^{-1}$  ( $\text{CH}_2$  def. vibr.) are given in Table 1. In most cases, the unicomponent catalysts give rise to polymers with a higher content of *cis* double bonds in the main chain. Only  $\text{WOCl}_4$  and the complex with the bulky 2,6-di-*t*-butylphenoxo ligand yield polymers with a higher content of *trans* double bonds.

The catalytic activities of all of the complexes strongly increase when they are combined with  $\text{Et}_2\text{AlCl}$  or  $\text{Bu}_4\text{Sn}$  (Table 2). Systems with  $\text{Et}_2\text{AlCl}$  are very efficient and yield the hard, insoluble polymer with a high content of *trans* double bonds. On the other hand, the combination of  $\text{WCl}_5(\text{O}-4\text{-}t\text{-Bu-C}_6\text{H}_4) + \text{Bu}_4\text{Sn}$  initiates less rapid polymerization, and the resulting polymer is soft, soluble and contains a low percentage of *trans* double bonds.

TABLE 2

Polymerization of DCPD by the systems with co-catalysts

| No. | Catalytic system  | Time (min) | Yield (%) | IR characterization ( $A_{973}/A_{755}/A_{1445}$ ) |
|-----|---|------------|-----------|--|
| 1   | $\text{WCl}_5(\text{O}-4\text{-t-Bu-C}_6\text{H}_4) + \text{Et}_2\text{AlCl}$ (1:4)         | 1          | ca. 100   | 1.64/0.58/1  |
| 2   | $\text{WCl}_4[\text{O}-\text{CH}(\text{CH}_2\text{Cl})_2]_2 + \text{Et}_2\text{AlCl}$ (1:3) | 1          | 90        | 2.04/0.43/1  |
| 3   | $\text{WCl}_5(\text{O}-4\text{-t-Bu-C}_6\text{H}_4) + \text{Bu}_4\text{Sn}$ (1:4)           | 30         | 30        | 0.92/1.38/1  |

Conditions: lab temp., benzene;  $[\text{W}^0] = 10 \text{ mmol l}^{-1}$ ; DCPD/catalyst = 150/1; time given above = reaction time.

## Discussion

Alkoxo and phenoxo groups in  $(\text{RO})_x\text{WCl}_{6-x}$  catalysts act as  $\pi$ -donors to the tungsten atom. For the system  $\text{W}(\text{OAr})_4\text{Cl}_2 + \text{EtAlCl}_2$ , Dodd and Rutt showed [6] that the rate of metathesis is enhanced by factors that can reduce the back-bonding from ligand to tungsten, and they concluded that carbene species, *i.e.*, catalytic active centres, are electrophilic in nature.

In our unicomponent catalysts, the substrate itself adopts the role of co-catalyst. This role consists in the reduction of tungsten to a lower oxidation state and in the formation of carbene ligand from DCPD coordinated to the tungsten atom. As mentioned above,  $\text{WCl}_6$  reacts with DCPD very quickly. The substitution of Cl atom in  $\text{WCl}_6$  by a less electronegative ligand must lead to a decrease in the tungsten reduction rate. This decrease is expected to become larger with increasing electron-donation from ligand to tungsten. If the requirement of electrophilicity of carbene species is correct and can be extended to our case, then the nature of the OR ligand influences both the rate of formation of carbenes and their activities. The increasing  $\pi$ -donation ability of ligands in the series  $-\text{O}-\text{CH}-(\text{CH}_2\text{Cl})_2 < -\text{O}-4\text{-Cl-C}_6\text{H}_4 < -\text{O}-4\text{-t-Bu-C}_6\text{H}_4$  gives a good explanation for differences in activity of  $\text{WCl}_5(\text{OR})$  catalysts. The low activity of the di-*t*-butylphenoxo derivative is probably due to the sterically hindered coordination of DCPD. The strongly depressed activity of  $\text{WCl}_4(\text{OR})_2$  compounds as unicomponent catalysts may be ascribed to their increased resistance toward reduction by DCPD; they exhibit, however, relatively high catalytic activities in combination with a reducing organometallic co-catalyst [9].

The copolymerization of norbornene and cyclopentene was studied by Ivin *et al.* [10]. The copolymerization parameters they found show that the incorporation of norbornene units into the copolymer is strongly preferred. This is in accord with our observation that ROMP of DCPD proceeds predominantly via opening of the norbornene ring. Polymer crosslinking occurs at later stages, probably as a result of a chain transfer by the polymer. Therefore, less active catalysts, *e.g.*, unicomponent ones, can provide linear or only slightly crosslinked polymers suitable for further modification (hydrogenation, etc.).

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