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# Ring-opening polymerization of cycloolefin induced by tungsten porphyrinates

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#### Abstract

Polymerization reactions of cyclopentene, cyclooctene and cyclododecene have been carried out in presence of catalytic systems based on tungsten tetraphenylporphyrinate, under inert atmosphere at room temperature, in aromatic solvents. The catalyst precursor was prepared by interaction of WCl<sub>6</sub> with free tetraphenylporphyrin in CCl<sub>4</sub> and characterized by spectroscopic methods (e.g. UV–Vis etc.). Spectroscopic studies on the interaction between the catalytic components or with the monomer, as well as kinetic results, molecular weight distribution and polymer microstructure indicated a high stability and efficiency of the catalytic systems employed. This catalyst allowed polyalkenamers with monomodal and narrow molecular weight distribution to be obtained. The polypentenamer displayed a block and/or alternate distribution of the carbon–carbon double bond dyads and high *trans* configuration. Data obtained under the above conditions gave information concerning the nature of active species during the initiation and propagation reactions.

Key words: cycloolefins; olefins; porphyrinates; ring opening; tungsten

# 1. Introduction

It is well known that metalloporphyrins, which include very important natural complexes, are highly effective catalysts for many reactions [1].

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Inoue and coworkers [2,3] found that Al and Zn porphyrins are excellent initiators for the living polymerization of a variety of monomers such as epoxides, lactones, lactides, acrylics and also for the copolymerization of epoxides, cyclic anhydrides and  $CO_2$ .

It is known that transition metals in the highest possible oxidation state are very active in ROMP of cycloolefins [4], e.g. W (VI). One crucial problem with most transition metal ROMP catalysts is the high reactivity of the catalysts with substrates that contain functional groups having heteroatoms such as O,S and N.

In this work we wish to report, for the first time, preliminary results on the synthesis, characterization and uses of tungsten tetraphenylporphyrinate (TPPWCl<sub>4</sub>) as a catalyst precursor in ring-opening metathesis polymerization of cycloolefins.

The present work focuses on kinetic results, molecular weight distribution and microstructure in ROMP of cyclopentene, cyclooctene and cyclododecene induced by TPPWCl<sub>4</sub>. Data on stability and efficiency of the catalytic systems are also presented.

#### 2. Experimental

#### 2.1. Starting materials

Cyclopentene was obtained from cyclopentanol by dehydration with  $H_3PO_4$  and subsequent distillation on highly effective column and stored over K–Na alloy (purity 99.9% VPC).

Cyclooctene (Merck), cyclododecene, dicyclopentadiene (Fluka) of commercial grade were stored over K-Na alloy and distilled under high vacuum.

WCl<sub>6</sub> was purified by removing volatile impurities under high vacuum and handled as described elsewhere [5].

TPPWCl<sub>4</sub> was obtained by equimolar reaction of WCl<sub>6</sub> and TPPH<sub>2</sub> in CCl<sub>4</sub> at refluxing temperature, for 24 h.

Commercial grade triisobutylaluminium (TIBA) was distilled and sealed under high vacuum.

Tetraisobutylaluminooxane (TIBAO) was prepared from TIBA and water [6].

#### 2.2. Polymerization reaction

The polymerization of cyclopentene, cyclooctene, cyclododecene were conducted according to a procedure reported elsewhere [5].

Concentration and molar ratio used were as follows: [monomer] = 4.8 mol/l;[TPPWCl<sub>4</sub>] = 1.10<sup>-3</sup> to 2.10<sup>-3</sup> mol/l; [TIBAO]/[W] = 2; [chloranil]/[W] = 1.

The polymerizations were carried out in toluene as solvent and the reaction times were from 1 to 24 h. Yields of polymer between 10–90% were obtained. Polymers were precipitated in methanol, filtered and dried, giving yields between 10% and 90%. The polymer microstructure was evaluated from <sup>13</sup>C NMR spectroscopy and the molecular weight was determined by viscosimetric measurements and gel permeation chromatography (GPC) using a Waters Assoc. (equipped with R 401 differential refractometer and 4  $\mu$ -Styragel

columns 500,  $10^3$ ,  $10^4$ ,  $10^5$  A) in THF at a flow rate of 1 cm<sup>3</sup>/min and calibrated on polystyrene standards.

## 2.3. ESR spectroscopic studies

ESR spectroscopic measurements of W paramagnetic species generated from tungsten porphyrinate and from tungsten porphyrinate and organoaluminium compounds in the presence of cycloolefins were carried out by the method previously described [7] using JES-MF-3X spectrometer operating in X-band frequency (9 GHz) using DPPH as the internal standard.

#### 3. Results and discussion

Tetraphenylporphyrinatotungsten tetrachloride (TPPWCl<sub>4</sub>) was prepared by equimolar reaction between WCl<sub>6</sub> and free tetraphenylporphyrin:



W atom displaces two hydrogen ions from the porphyrin ligand and forms four coordinative donor-acceptor bonds with nitrogen atoms. Electronic absorption spectra of a TPPWCl<sub>4</sub>, as a rich source of information about coordination, indicated a Soret (418 nm) and two visible bands, called  $\alpha$  and  $\beta$ , at 608 and 662 nm. The wavelength of the  $\alpha$ -band appears to be related to the band I (646) and III (546) in the free TPPH<sub>2</sub> spectrum and the  $\beta$  band appears to be related to the bands II (585) and IV (515) (Fig. 1).

Typical IR spectra of TPPWCl<sub>4</sub> as presented in Fig. 2 indicated vibration for W–Cl bond (415, 365, 350, 240 cm<sup>-1</sup>) and absence of a specific band of deformation for N–H bond at 3400–3600 cm<sup>-1</sup>.

ESR investigation on the TPPWCl<sub>4</sub> in CCl<sub>4</sub> indicates that paramagnetic species are present. Three resonance lines (Fig. 3) are located at  $g = 2.0040 \pm 0.0005$ ,  $g=1.9670\pm0.0005$  and  $g=1.8815\pm0.0005$  respectively. The first two lines are ascribed to free radicals [7]. The strongest resonance located at g=1.8815 with a line width of about 122 Gs, has been ascribed to W ions, with an electronic configuration analogous to W (V) [7]. The system cyclopentene/TPPWCl<sub>4</sub>/TIBAO presents four resonance lines. The lines associated with free radicals are not significantly affected, the intensity of the resonance line located at g=1.8815 is significantly reduced and a resonance line located at



Fig. 1. Absorption spectra for TPPWCl<sub>4</sub> ( $\cdots$ ) and TPPH<sub>2</sub> (----).





g = 1.8010 with a peak to peak linewidth of about  $60 \pm 2$  Gs is noticed. This line has been tentatively assigned to the modification of ligands by alkylation of W.

Kinetic measurements evidenced that the polymerization of cyclopentene in the presence of TPPWCl<sub>4</sub>/TIBAO, at room temperature, proceeds in 1.5 h. Much higher rates are obtained in the presence of catalytic amounts of chloranil (Fig. 4).

GPC analysis (Fig. 5, ) indicated a monomodal and narrow MWD for the polymerization of cyclopentene, with a PDI from 1.157 to 1.246.

Cyclooctene is also polymerized with this catalytic system and time evolution and  $M_w/M_n$  evolution in ROMP is presented in Fig. 6.

GPC analysis (Fig. 7) also indicates monomodal and narrow MWD.

The TPPWCl<sub>4</sub>/TIBAO system has also been found to be active in cyclododecene poly-



Fig. 3. ESR spectra of TPPWCl<sub>4</sub>/CCl<sub>4</sub> (1), TPPWCl<sub>4</sub>/TIBAO (2), TPPWCl<sub>4</sub>/CP/TIBAO (3).



Fig. 4. Time evolution and PDI in ROMP of cyclopentene initiated by TPPWCl<sub>4</sub>/TIBAO. ( $\bigcirc$ ) [TPPWCl<sub>4</sub>] = 2.10<sup>-3</sup> mol/1, [CP] = 3.43 mol/1, [TPPWCl<sub>4</sub>]/[TIBAO] = 1/2, [TPPWCl<sub>4</sub>]/[chloranil] = 1; ( $\diamondsuit$ ) [TPPWCl<sub>4</sub>] = 2.10<sup>-3</sup> mol/1, [CP] = 3.43 mol/1, [TPPWCl<sub>4</sub>]/[TIBAO] = 1/2; ( $\Box$ ) [TPPWCl<sub>4</sub>] = 1.10<sup>-3</sup> mol/1, [CP] = 3.43 mol/1, [TPPWCl<sub>4</sub>] = 1/2.



Fig. 5. GPC curves of polypentenamers prepared with TPPWCl<sub>4</sub>/TIBAO system. (1) Time 15 min, D = 1.157; (2) time 90 min, D = 1.246.



Fig. 6. Time evolution and PDI of cyclooctene polymerization initiated by TPPWCl<sub>4</sub>/TIBAO system. Conditions as in Fig. 4.



Fig. 7. GPC curves of polyoctenamers. (1) Time 10 min, D = 1.140; (2) time 1 h, D = 1.167; (3) time 10 h, D = 1.22.



Fig. 8. Time evolution of cyclododecene polymerization induced by TPPWCl<sub>4</sub>/TIBAO system.

merization (Fig. 8). Under the same conditions, the following order of reactivity was obtained: cyclopentene > cyclododecene > cyclooctene. With this catalytic system it is possible to prepare well-defined block copolymers. Block copolymers of dicyclopentadiene-cyclopentene and dicyclopentadiene-cyclooctene have been obtained as illustrated in Fig. 9.

From polydicyclopentadiene synthesized with TPPWCl<sub>4</sub> with  $M_n = 105000$  block copolymers were obtained with cyclopentene (yield 40%) and cyclooctene (yield 30%) both having narrow MWD.

Analyses of the polymer microstructure indicated that the catalytic systems derived from



Fig. 9. GPC curves for (1) polydicyclopentadiene, (2) block-copolymer of polydicyclopentadiene–polypentenamer and (3) block-copolymer of polydicyclopentadiene–polyoctenamer.

Table 1 Microstructure of polypentenamers obtained with TPPWCl<sub>4</sub>/TIBAO system

Run no.	Olefin	Yield (%)	cis-Product (%)	R	Distribution
1	cyclopentene	10	23.07	0.68	alternate
	• •	18	19.88	0.73	alternate
		23	19.21	0.73	alternate
		45	18.68	0.74	alternate

Table 2

Microstructure of polyalkenamers obtained with TPPWCl<sub>4</sub>/TIBAO system

Run no.	Olefin	Yield (%)	cis-Product (%)	trans-Product (%)
2	cyclooctene	10	45.40	54.60
		25	44.20	55.80
		60	35.29	64.71
3	cyclododecene	10	45.45	54.55
		50	33.30	66.70

TPPWCl<sub>4</sub> and TIBAO gave mainly *trans*-configuration of the double bond and surprisingly an alternate distribution of the carbon–carbon double bond dyads (Table 1 and Table 2). For example polypentenamers obtained with TPPWCl<sub>4</sub> have about 80% *trans* (determined by <sup>13</sup>C NMR spectroscopy) and from the relation:

$$R = \frac{(P_{\rm cc} + P_{\rm tt})}{(P_{\rm tc} + P_{\rm ct})^2} = 0.72 > 0.25,$$

where  $P_{cc}$ ,  $P_{tt}$ ,  $P_{ct}$ ,  $P_{tc}$  = population of *cis-cis*, *trans-trans*, *cis-trans* and dyads (calculated



Fig. 10. Expanded <sup>13</sup>C-NMR spectrum (methylenic region,  $25 < \delta$  (ppm) < 33) of polypentenamer with 80.66% *trans* obtained with TPPWCl<sub>4</sub>.



Fig. 11. Possible structure of active species.

from  $\beta$  CH<sub>2</sub> region [8]) the *cis/trans* double bond distribution was largely alternate (Fig. 10).

A possible configuration for the initiation and propagation species involving the W atom in a lower oxidation state is presented in Fig. 11. It is obvious that the polymer chain and the cycloolefin will adopt a favorable position to allow minimum interaction in leading to a *trans*-metallacyclobutane intermediate.

It is of interest that this catalytic system allowed polyalkenamers with a monomodal narrow MWD to be obtained instead of a bimodal one as previously reported with other tungsten catalytic systems [9,10]. As oligomers or other low molecular weight compounds have not been observed by our experimental technique, it is quite probable that this type of catalyst to avoid the secondary metathesis reactions (i.e. back-biting) frequently encountered with the conventional W-based catalytic systems.

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