

Polarographic studies of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}$ and EPR studies of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}/\text{styrene}$ systems

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Abstract

Cyclopentadienyl-titanium complexes containing $-\text{OC}_6\text{H}_4\text{X}$ ligands ($\text{X} = \text{NO}_2, \text{Cl}, \text{H}, \text{C}(\text{CH}_3)_3, \text{OCH}_3$) were synthesized. The “X” substituents at the phenoxy ligands have different electron donor properties, which are described by Hammett’s factors.

Mixtures of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})$ and MAO were investigated by polarography. The amount of Ti(III) ions have been noticed.

EPR spectra were recorded for mixtures of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})$ with MAO and styrene. The shape and the parameters of the EPR spectra were found to be related to the nature of $-\text{OC}_6\text{H}_4\text{X-p}$ ligands. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Research works on syndiotactic polymerization of styrene over titanium catalysts are based on the presumption that the Ti(III) ion bonded to cyclopentadienyl ligand is the active form of the catalyst [1–3]. Therefore, the amount of such ions in the reaction system should decide about its efficiency.

Two forms of the catalysts are important, the first one composed during contact with the monomer, and the second one generated during the chain transfer at the end of the polymerization. If these forms initiate the growth of polymer chain, it will be possible to

carry out reactions at lower catalyst concentration. The time of reaction could also be prolonged.

Information about the active form of the catalyst can be deduced from EPR analyses. Chien et al. [4] have determined the active oxidation state of titanium in the $\text{CpTi}(\text{O}i\text{Bu})_3/\text{MAO}$ catalyst by EPR and redox titration. They have found all the catalytic species are trivalent Ti. The Ti(IV):Ti(III):Ti(II) ratio calculated from polarographic data was different before and after addition of styrene.

The EPR measurements of the titanium catalysts showed some complexes of Ti(III) to have hydrogen ligands and the titanium ion’s unpaired electron of to interact with aluminum nuclei. After addition of styrene, the titanium hydride complex continued to exist, but the unpaired electrons interacted with two aluminum nuclei. These forms are catalytically inactive.

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The shape of the EPR spectra was related to the titanium ion concentration and the Al:Ti ratio in the solution [4,5].

Ligands which are attached to titanium ion, also affect the shape of the EPR spectra, the “g” factor and the amount of Ti(III) ions [8,9]. But these studies have not shown exactly, how ligands electron donating properties affect the EPR values.

To prove this influence, we synthesized cyclopentadienyl-titanium complexes containing $-\text{OC}_6\text{H}_4\text{X}$ ligands (X = NO_2 , Cl, H, CH_3 , $\text{C}(\text{CH}_3)_3$, OCH_3); the substituents, designated as “X”, have electron donor properties, which can be described by Hammett’s factors.

This paper sets out to describe the results of our investigations on $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}$ catalysts. The amounts of Ti(III) ions in the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}$ catalysts were found to be determined by $-\text{OC}_6\text{H}_4\text{X}$ ligands. The parameters and the shape of the EPR spectra recorded for $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}/\text{styrene}$ systems were also found to depend upon the kind of the ligand.

2. Experimental

Polarography was used to describe $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}$ catalytic systems. WITCO’s 10% solution of MAO in toluene was used. Titanium complexes were prepared according to the literature [5,6], and their purity was determined by $^1\text{H-NMR}$ spectra. The NMR (C_6D_6) data for these compounds are as follows: $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{NO}_2\text{-p})$ δ : 7.52 (4H, d), 6.23 (5H, s); $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{Cl-p})$ δ : 6.92 (2H, d), 6.51 (5H, d), 6.01 (5H, s); $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{H-p})$ δ : 6.60 – 6.38 (5H, m), 6.06 (5H, s); $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{CH}_3\text{-p})$ δ : 6.64 – 6.53 (4H, m), 5.79 (5H, s), 1.83 (3H, s); $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{OCH}_3\text{-p})$ δ : 6.62 – 6.40 (4H, m), 5.94 (5H, s), 2.8 (3H, s); $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{C}(\text{CH}_3)_3\text{-p})$ δ : 6.67 – 6.41 (4H, m), 5.98 (5H, s), 1.19 (9H, s).

Polarographic analyses were performed on $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}$ samples in toluene (Ti 1 mmol; Al:Ti ratio, 300:1) at room temperature according to the literature [4]. Salts of iron were used to titrate titanium ions at different oxidation states. $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ was used to make the calibration curve. Mixtures of titanium complexes were titrated with FeCl_3 . Reduced iron ions were determined

polarographically [4]. Analyses were performed with a “Radelkis” apparatus.

The EPR spectra of $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}/\text{styrene}$ were recorded 24 h after styrene had been added (Al:Ti:styrene ratio was 300:1:2000, 1 ppm Ti) at room temperature, at X band with modulation 0.16 mT on a “Wroclaw 200” apparatus. After this period of time, the EPR tubes contained the solids having unreacted styrene occluded there in and the solvent (toluene from the solution of MAO).

3. Results and discussion

Our polarographic studies on the $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}$ systems showed Ti(IV), Ti(III), and Ti(II) ions to occur in the resulting mixture in amounts depending upon the kind of the substituent in the phenoxy ligand (Table 1). Hammett’s factors (σ) for the substituents mentioned are also listed in the Table 1 [7].

The Ti(III) content in the system was found to rise as electron donor properties of X substituents from 20% (NO_2 substituent) to 80% (OCH_3 substituent). The Ti(II) content did not exceed 20% in any studied sample. The Ti(III) content is seen to be well correlated with the values of Hammett’s factor (Fig. 1).

The structure of the present complexes is similar to that described in the literature for other monocyclopentadienyl-titanium complexes used as catalysts in syndiotactic polymerization of styrene [1,7]. Thus, we can assume the Ti(III) ions to have formed in reactions (1) and (2), analogous to the reactions described in the literature [1].

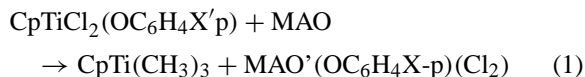


Table 1
Percentage content of Ti(IV), Ti(III) and Ti(II) ions at $\text{CpTiCl}_2(\text{OC}_6\text{H}_4\text{X-p})/\text{MAO}$ system

Ti ion	X substituent					
	NO_2	Cl	H	CH_3	$\text{C}(\text{CH}_3)_3$	OCH_3
Ti(IV)	65	35	25	10	15	0
Ti(III)	20	55	65	75	75	80
Ti(II)	15	10	10	15	10	20
σ	1.24	0.23	0	-0.17	-	-0.27

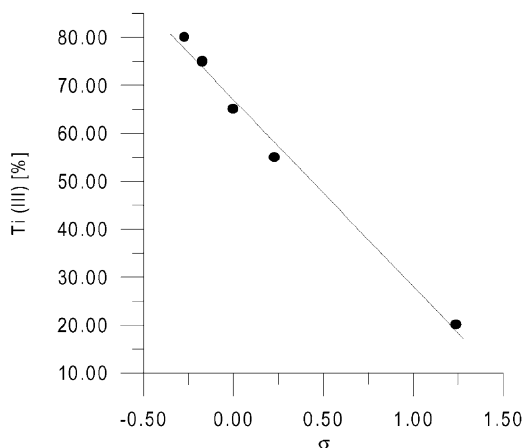
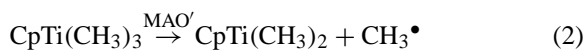


Fig. 1. Content of Ti(III) ions in CpTiCl₂(OC₆H₄X-p)/MAO system as the function of the Hammett's factors.



In reaction (1), the complexes of Ti(IV) are alkylated to cyclopentadienyl-trimethyltitanium. Then these compounds decompose to produce cyclopentadienyl-dimethyltitanium (III) (reaction (2)). At the same time, a “new MAO”, i.e. MAO'(OC₆H₄X-p)(Cl₂) is formed.

The phenoxy ligand containing substituents of different electron donor-acceptor properties should impart new properties to the resulting “new aluminoxanes”, because phenoxy ligands abstracted from the titanium ion exist in “new MAO” and change the specific Lewis acidity of the one.

The present results suggest that alkylation of Ti(IV) complexes, which contain phenoxy ligands with the electron donor “X” substituents, is easier. Thus, more CpTi(CH₃)₃ derivative is produced. It can be generalized that every electron donor ligand X in CpTiX₃ compounds will accelerate this alkylation.

EPR spectra were recorded for the CpTiCl₂(OC₆H₄X-p)/MAO/styrene systems having the composition of our typical reaction system (Fig. 2).

To establish the stable structures formed by titanium at the end of the polymerization reaction we recorded the EPR spectra after 24 h. The conversion of styrene was higher than 90%. We assume that the final forms of titanium exist near the modified MAO. The spectra

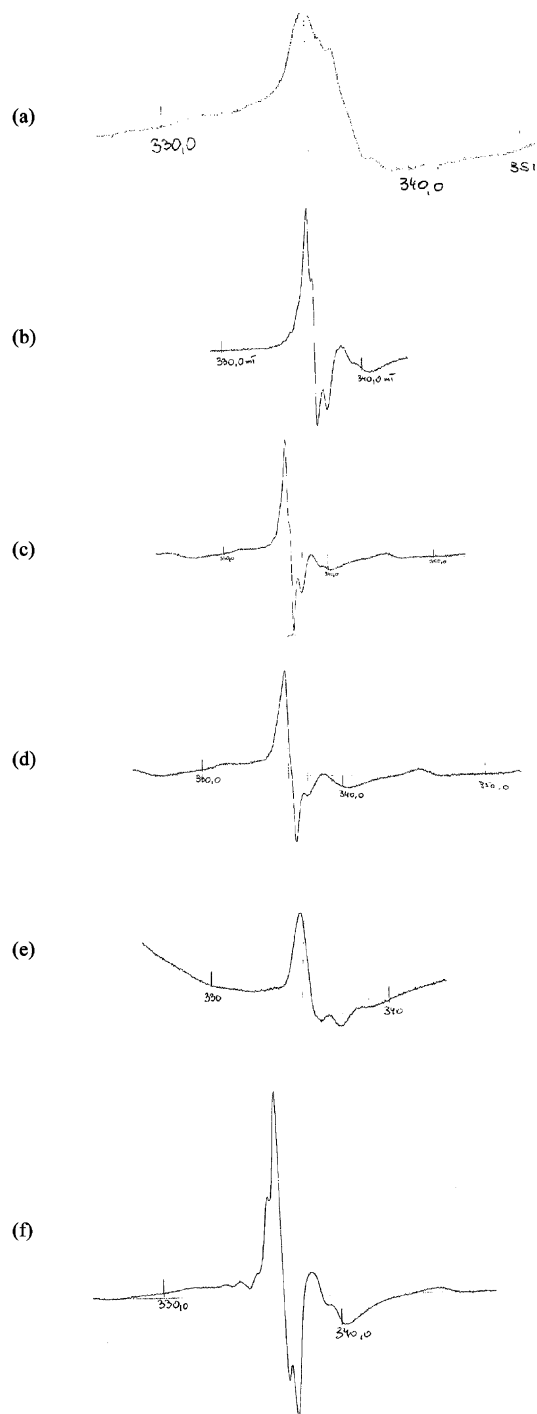


Fig. 2. EPR spectra recorded for CpTiCl₂(OC₆H₄X-p)/MAO/styrene systems, where X is: (a) OCH₃; (b) Cl; (c) H; (d) CH₃; (e) NO₂ and (f) tBu.

interact with the magnetic field of the titanium ions, but do not form any bonds.

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