# Polystyrene with half-titanocene/MAO catalysts: Influence of 2,6-diisopropylphenol

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## A B S T R A C T

Styrene polymerization was carried out by a simple half-titanocene complex [cyclopentadienyltitanium trichloride] ($CpTiCl_3$) and pentamethyl [cyclopentadienyltitanium trichloride] ($Cp^*TiCl_3$) combined with methylaluminoxane (MAO) as a cocatalyst. The effects of addition of 2,6-diisopropylphenol on the catalytic activity of the above catalytic systems and the microstructure of the resulting polymer were investigated. The results of the above experiments showed that the addition of the 2,6-diisopropylphenol changed the catalytic performance of the above catalytic systems, in terms of catalytic activity of the metal complexes and microstructure, molecular weight and molecular weight distribution of polystyrene synthesized. The yields of polystyrene of the above polymerization reactions indicated that the 2,6-diisopropylphenol enhanced the catalytic activity of both the $CpTiCl_3$/MAO and $Cp^*TiCl_3$/MAO catalyst systems. Further Soxhlet extraction of the polymer was conducted by boiling acetone for 6 h to get pure syndiotactic polystyrene. The microstructure of polystyrene obtained by the above polymerization reactions was investigated by $^{13}C$ NMR, GPC and DSC. Results indicated the formation of syndiotactic polystyrene in the absence of phenol and in low concentration of phenol. On the other hand, in the presence of excess phenol, the polystyrene produced was found to be completely atactic in nature. The appearance of monomodal peaks and narrow polydispersity in the GPC results of polystyrenes obtained in all the above polymerizations indicated that the polymerization was only coordination in nature.

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## 1. Introduction

In recent years, group IV metallocene complexes have been extensively studied as homogeneous catalysts for olefin polymerization in the fields of organometallic chemistry, catalysis and polymer science [1–5]. Stereospecific olefin polymerization by metallocene catalysts can produce polymers with new microstructures and has thus attracted extensive attention in both academic and industrial communities [6–10]. Syndiotactic polystyrene (sPS) was first synthesized by Ishihara et al. with mono cyclopentadienyl titanium catalysts activated with methylaluminoxane (MAO) [11,12]. Subsequently, a large number of mono cyclopentadienyl titanium complexes were synthesized and studied to obtain better catalysts [13–25].

It has been widely believed that the important key issues for a successful design of an efficient transition metal catalyst for styrene polymerizations are as follows: (a) catalytic activity, (b) molecular weight and molecular weight distribution, and (c) stereo regularity. With the great success of group IV metallocene polymerization catalysts, an intense interest in the development of related homogeneous catalysts supported by Cp and non-Cp ligand systems has been developed. A variety of non-bridged half-metallocenes containing anionic ancillary donor ligands have been examined in olefin polymerization [26].

Nomura et al. reported that half-titanocene having aryloxy ligand exhibits the excellent catalytic activity for styrene polymerization and for ethylene and styrene copolymerization [27–29]. It was obvious that type of the ligand influenced the catalytic activity. However, the mechanism of activation of catalyst and the role of aryloxy ligand have remained unclear. The mechanism of syndiospecific styrene polymerization has been extensively studied already, and the cationic or neutral trivalent Ti(III) has been proposed as an active species for syndiospecific coordination polymerization by a half-titanocene catalyst system [26,30–33]. In the cationic Ti(III) model, the aryloxy ligand seemingly separates from the titanium center, while one ligand can coordinate to the

titanium center in addition to the Cp ligand in the neutral Ti(III) model. Therefore, it is meaningful to elucidate how the aryloxy ligand acts during polymerization.

In this paper, we would like to supply information about the role of the aryloxy ligand in the syndiospecific styrene polymerization. The styrene polymerization was carried out by the simple half-titanocene complexes $CpTiCl_3$ and [pentamethylcyclopentadienyltitanium trichloride] ($Cp^*TiCl_3$) combined with MAO as a cocatalyst. The effects of addition of 2,6-diisopropylphenol derivatives on the catalytic activity and on the microstructure of polymer were investigated by characterization of the polymer by $^{13}C$ NMR, GPC and DSC.

## 2. Experimental

### 2.1. General procedures

All manipulations involving air and moisture sensitive compounds were carried out under a nitrogen (ultrahigh purity) atmosphere using standard Schlenk techniques. Toluene were refluxed under nitrogen over calcium hydride and distilled, then stored under nitrogen atmosphere. Triisobutylaluminum-modified methylaluminoxane (MMAO, 6.6 wt.% in toluene) purchased from Tosoh-Finechem Co. was used without further purification. $CpTiCl_3$ and $Cp^*TiCl_3$ were purchased from Strem. Styrene was dried with calcium hydride and distilled under reduced pressure at room temperature before use.

### 2.2. Polymerization of styrene

Styrene polymerization experiments were carried out in a three-necked 100 mL round bottom flask with a magnetic stirrer. After degassing, the flask was purged with nitrogen and 25 mL of toluene, an appropriate amount of the 2,6-diisopropylphenol, and 6 mL of MMAO were added intoit under nitrogen atmosphere. The mixture was then stirred at room temperature for 10 min. Then 6 mL of freshly distilled styrene was added. The polymerization is started by addition of the half-titanocene in toluene solution, and the polymerization is allowed to continue at room temperature. The polymerization is terminated by the addition of 10% HCl in methanol. The precipitated polymer was washed three times with methanol and dried at 60 °C in vacuo to a constant weight.

Further Soxhlet extraction of the polymer was conducted by boiling acetone for 6 h.

### 2.3. Analysis

$^1H$ and $^{13}C$ NMR spectra were recorded at 120 °C on a JEOL JNM-LA600 spectrometer operated at 600 and 150 MHz in pulse Fourier transform mode, respectively. Sample solutions are made up in tetrachloroethane-$d_2$ to 10% by weight. The peaks of tetrachloroethane-$d_2$ ($^1H$ = 5.91 ppm, $^{13}C$ central peak = 74.47 ppm) were used as internal references. The melting transition temperature (Tm) and the glass transition temperature (Tg) of the polystyrene were determined by differential scanning calorimeter (DSC) on a Mac science DSC3100SR at a heating rate of 10 °C/min. Number average molecular weights ($M_n$), weight average molecular weights ($M_w$) and gel permeation chromatography (GPC) measured polydispersity (PD) of polymers were found at 120 °C on a Polymer Laboratories PL GPC-220 using trichlorobenzene as a solvent. The calibration was done by Polymer Laboratories detector software Cirrus with PS-standard.

## 3. Results and discussions

The results of styrene polymerization catalyzed by $CpTiCl_3$ and $Cp^*TiCl_3$ combined with MAO under different conditions and further Soxhlet extraction of the polymer are summarized in Table 1. It is known that MAO has been the first highly effective activator of metallocene catalysts. But MAO solutions always contain "free" trimethylaluminum (TMA) in equilibrium with the oligomeric part. Being a reducing agent, TMA easily forms Me-bridged dinuclear species with transition metal complexes which are believed to be catalytically inactive and to promote chain transfer with some catalysts to a point that results in the formation of oligomers rather than of high polymers.

A previous research report [34] shows that the controlled addition of a proper amount of sterically hindered phenol to MAO solutions is a facile and highly effective way to trap "free" TMA in MAO. It is also known that modification of Al trialkyls can be easily done by reaction with phenols in 1:1 to 1:2 mol ratios [35,36] and this can be used as an effective means to decrease the reactivity of TMA. The resulting MAO/phenol reaction product can activate equally well the dichloro-precursors of a metallocene and a "post-metallocene" catalyst, and its use in polymerization (even in the presence of excess free phenol) ended up with a higher catalyst productivity, polymer stereoregularity, and/or average molecular mass compared with such values for MAO alone [34].

In this work 2,6-diisopropylphenol was added to MAO/toluene solution before introduction of styrene and half-titanocene. This mixture was then kept stirring for 10 min at ambient temperature so that aluminum phenoxide formed in situ. In order to investigate the effect of the 2,6-diisopropylphenol, we changed the concentration of the phenol from 0 to 10 equiv. versus Ti. As can be seen from Table 1, the addition of the 2,6-diisopropylphenol changed catalytic performance, in terms of catalytic activity, microstructure, and molecular weight and molecular weight distribution of the produced polystyrene.

**Table 1**
Styrene polymerization with half-titanocene/MAO catalyst in the presence of 2,6-diisopropylphenol[a].

| Run | Catalyst | Phenol (μmol) | Activity (kg-PS/(mmol-Ti h)) | Tacticity[b] (%) | Tg/Tm[c] (°C) | $M_n$[d] | $M_w/M_n$[d] | SI[e] (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | $CpTiCl_3$ | 0 | 9.05 | syn | 127/213 | 3280 | 1.34 | 46 |
| 2 | $CpTiCl_3$ | 300 | 10.05 | syn | 105/228 | 2640 | 1.22 | – |
| 3 | $CpTiCl_3$ | 600 | 11.50 | syn | 114/210 | 2570 | 1.31 | 71 |
| 4 | $CpTiCl_3$ | 3000 | 14.02 | ata | 80/n.d. | 3130 | 1.59 | <1 |
| 5 | $Cp^*TiCl_3$ | 0 | Less | – | – | – | – | – |
| 6 | $Cp^*TiCl_3$ | 300 | Less | – | – | – | – | – |
| 7 | $Cp^*TiCl_3$ | 600 | 0.23 | syn | 89/263 | 6400 | 2.18 | – |
| 8 | $Cp^*TiCl_3$ | 3000 | 11.55 | ata | 86/n.d. | 2940 | 1.55 | <1 |
| 9[f] | – | 3000 | 0 | – | – | – | – | – |

[a] Polymerization conditions: Ti = 300 μmol; Al = 12.8 mmol; styrene = 6 mL; solvent = toluene; time = 180 min; temp. = rt.
[b] Stereoregularity of polymer determined by $^{13}C$ NMR.
[c] Glass transition temperature (Tg) and melting point (Tm) of polymer determined by DSC.
[d] Number average molecular weight and polydispersity determined by GPC.
[e] Syndiotactic index: boiling acetone insoluble part.
[f] Control run without Ti complex [41].