Available online at www.sciencedirect.com
SCIENCE DIRECT®
European Polymer Journal 41 (2005) 115–120
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

# Polymerization of vinyl chloride catalyzed by a titanium complex with an anionic oxygen tripod ligand

Jun-Ting Xu *, Qi Wang, Fei Wu, Zhi-Qiang Fan

*Department of Polymer Science and Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, PR China*

Received 11 May 2004; received in revised form 25 July 2004; accepted 7 August 2004
Available online 6 October 2004

---

## Abstract

Poly(vinyl chloride) (PVC) was prepared using a titanium complex with an anionic oxygen tripod ligand $[\mathrm{CpCo}\{\mathrm{P(O)(OEt)_2}\}_3]^-$ ($L_{\mathrm{OEt}}^{-}$) as catalyst and methyl aluminoxane (MAO) as cocatalyst. The polymerization behavior was compared with that of pentamethyl cyclopentadienyl titanium trichloride ($\mathrm{Me_5CpTiCl_3}$). It is observed that $\mathrm{L_{OEt}}$-$\mathrm{TiCl_3}$ can polymerize vinyl chloride with activity comparable to that of $\mathrm{Me_5CpTiCl_3}$. The PVC samples prepared with $\mathrm{L_{OEt}TiCl_3}$/MAO exhibit bimodal molecular weight distribution and the fraction of high molecular weight peak decreases with polymerization temperature. The microstructure and thermal decomposition of the PVC obtained were studied. Five types of structural defect were detected by $^1$H-NMR. Only saturated structural defects are found at low polymerization temperature, but at high polymerization temperature unsaturated structural defects, possibly resulting from dehydrochlorination of the saturated structural defects, appear as well. No head-to-head structural defect is observed. $^{13}$C-NMR shows that the PVC prepared by $\mathrm{L_{OEt}TiCl_3}$ has an atactic stereostructure. Compared with the PVC from radical polymerization and anionic polymerization, the PVC samples prepared with $\mathrm{L_{OEt}TiCl_3}$ show improved thermal stability.

*Keywords:* Poly(vinyl chloride); Ti complex; Structural defects; Thermal stability

---

## 1. Introduction

Currently most of the poly(vinyl chloride) is produced by radical polymerization. The obtained PVC usually contains lots of structural defects, such as head-to-head units, tertiary chlorines at branched carbons and chlorine atoms adjacent to internal double bonds, which are generally believed to be the origin of the poor thermal stability of PVC [1,2]. PVC can also be prepared by anionic polymerization [3–7] or coordination copolymerization [8,9]. Metallocene is a type of catalyst developed in 1990s and has been widely used in polymerization of olefin as well as some polar monomers [10–14]. By regulating the ligand structure in metallocenes, microstructure of the polymer including stereo-defects and regio-defects can be readily controlled [15,16]. Recently, some authors paid special attention to polymerization of vinyl chloride initiated by metallocene catalysts [17–23], and hope to obtain PVC with different chain structure and with improved thermal stability. Nevertheless, the polymerization mechanism of vinyl chloride catalyzed by metallocene is still unclear and controversial. Jordan et al. used 1,2-bis(indenyl)ethylene dimethyl zirconium as catalyst to polymerize vinyl

---

* Corresponding author. Tel./fax: +86 571 879 52400.
*E-mail address:* xujt@zju.edu.cn (J.-T. Xu).

0014-3057/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2004.08.010

chloride [17], but they found that this catalyst could cause dechlorination of the monomer and only propylene oligomer was obtained. They also investigated polymerization of vinyl chloride using $CpMe_5TiCl_3$ as catalyst in the presence of MAO and observed a free radical polymerization mechanism [19], but the source of initiating radicals was unknown. Nagy et al. also believed that photo-polymerization of vinyl chloride in the presence of metallocene and MAO is a free radical mechanism [24]. However, Endo et al. systemically studied polymerization of vinyl chloride using a series of haftitanocene as catalysts [20–23], and the free radical mechanism was excluded since addition of free radical scavenger had little effect on polymerization. The PVC prepared by half-titanocene catalysts is atactic, but it still exhibits some differences in other structural defects from that obtained by radical polymerization. For example, no branching structure and no head-to-head structure was detected by Endo and Saitoh [20,23]. In the present work, a titanium complex containing an anionic oxygen tripod ligand $[CpCo\{P(O)(OEt)_2\}_3]^-$ was used as catalyst for polymerization of vinyl chloride and the microstructure of PVC obtained was studied.

## 2. Experimental

### 2.1. Materials

Industrial grade vinyl chloride monomer was supplied by Hangzhou Electrochemical Factory (Hangzhou, China) and was purified with $CaH_2$ and silica to remove water and other unsaturated impurities. The solvent, $CH_2Cl_2$ for polymerization was refluxed with $P_2O_5$ before use. The catalyst $L_{OEt}TiCl_3$ was kindly donated by Dr. W. H. Leung in The Hong Kong University of Science and Technology. Preparation of $L_{OEt}TiCl_3$ has been described elsewhere [25]. The structures of $L^-_{OEt}$ anionic oxygen tripod ligand and $L_{OEt}TiCl_3$ catalyst are shown in Fig. 1. $Me_5CpTiCl_3$ was provided by Shanghai Research Institute of Petrochemical Technology. The cocatalyst methyl aluminoxane (MAO) was purchased from Albemarle Corporation.

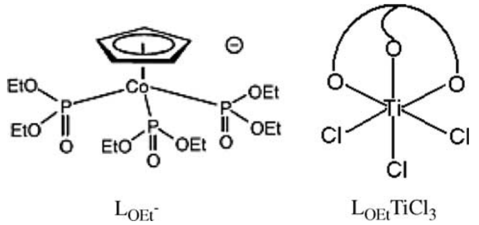

Fig. 1. Structures of $L^-_{OEt}$ anionic ligand and $L_{OEt}TiCl_3$ catalyst.

### 2.2. Polymerization

Polymerization of vinyl chloride was conducted in a sealed glass tube. Prescribed amount of solvent, MAO, catalyst and vinyl chloride were added in the said order, and then the glass tube was sealed. Polymerization was terminated by addition of methanol containing a small amount of hydrochloric acid. The precipitated product was filtrated and dried in vacuum.

### 2.3. Characterization of PVC

$^1H$- and $^{13}C$-NMR spectra were recorded on a Bruker DMX-500 spectrometer at 80 °C by using *o*-benzene dichloride as solvent. Molecular weight and molecular weight distribution were measured on a Waters 150C gel permeation chromatography (GPC) at 30° C with tetrahydrofuran (THF) as solvent. Thermal gravity analysis (TGA) was performed on a NETZSCH STA 409PG/PC in the temperature range of 30–600 °C. The heating rate applied was 8 °C/min.

## 3. Results and discussion

### 3.1. Polymerization results

Table 1 summarizes the results of polymerization of vinyl chloride catalyzed by $L_{OEt}TiCl_3$/MAO and $CpMe_5TiCl_3$/MAO. The data in Table 1 show that $L_{OEt}TiCl_3$ can polymerize vinyl chloride and the catalytic activity is comparable to that of $CpMe_5TiCl_3$. Increase in Al/Ti ratio and polymerization temperature drastically reduces the catalytic activity. The number-average molecular weight of the PVC prepared by $L_{OEt}TiCl_3$/MAO is in the order of ten thousand. The molecular weight decreases as polymerization temperature increases. The molecular weight distribution of PVC prepared at low Al/Ti ratio is about 2.0, similar to that from radical polymerization. However, close examination of the GPC curves reveals that there are two GPC peaks, one minor peak corresponding to high molecular weight and one major peak corresponding to low molecular weight (Fig. 2). Similar GPC result is obtained for PVC prepared with $CpMe_5TiCl_3$ MAO. This indicates that there may exist more than one type of active site in both catalytic systems at lower polymerization temperature, though the polymerization reaction is homogeneous. With the increase of polymerization temperature, the minor peak becomes smaller and smaller, showing that the active site producing high molecular weight fraction disappears or becomes the similar to the other one at higher polymerization temperature. At high Al/Ti ratio, the molecular weight distribution becomes remarkably broader.