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Synthesis and Characterization of Niobium and Tantalum Complexes with Bidentate Ligand and its use in Ring Opening Polymerization of ε-Caprolactone

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Reaction of two equivalents of the bidentate 2,2'-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$OH]$_2$ with one equivalent of niobium pentachloride gave the complex Nb{2,2'-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$O]$_2$}$_2$ (**1**) . Similar use of two equivalents of the same ligand with one equivalents tantalum pentachloride afforded Ta{2,2'-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$O]$_2$}$_2$ (**2**). The molecular structure of complexes **1** and **2** have been characterized by IR and ^{1}H NMR. Both complexes were investigated as catalysts for polymerization of cyclic esters (ε-caprolactone) with no solvent at various time at 110 °C. In all cases the polymer produced was of high yield percent.

Keywords: Niobium(V), Tantalum(V), Phenolate, ε-Caprolactone, Ring opening polymerization.

INTRODUCTION

Biodegradable polymeric material produced *via* ring opening polymerization (ROP) of ε-caprolactone continues to catch much attention by reason of a wide range of applications [1,2]. A variety of catalysts have been used as initiators for ring opening polymerization and coordination chemistry shows a significant role in this process, the use of niobium and tantalum compounds received more attention due to no toxicity related with these metals. According to the literature a few papers published on these metals complexes as catalysts toward polymerization of lactide, lactone or ethylene [3-6]. The use of Schiff base ligation has received more interest because of easy to prepare [7] and versatile applications of Schiff base and their complexes as biological activity, antifungal properties, anticancer properties, application in modern technologies, application in synthesis and chemical analysis [8-13].

In this paper, two complexes of niobium and tantalum were synthesized, characterized and their catalytic behaviour was investigated. As compared with one equivalent of 2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$OH]$_2$ prepared by Redshaw *et al*. [14] and Müller *et al.* [15], we have found that by employing two equivalent of 2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$OH]$_2$ ligand can be beneficial in term of control of polymerization.

EXPERIMENTAL

Dried environment was carried out throughout the experiment. Solvents were dried before use. Infrared spctra were recorded using Nicolet Avatar 360 FTIR spectrometer. ^{1}H NMR were recorded at 400 MHz in a (VXR 400 S) spectrometer.

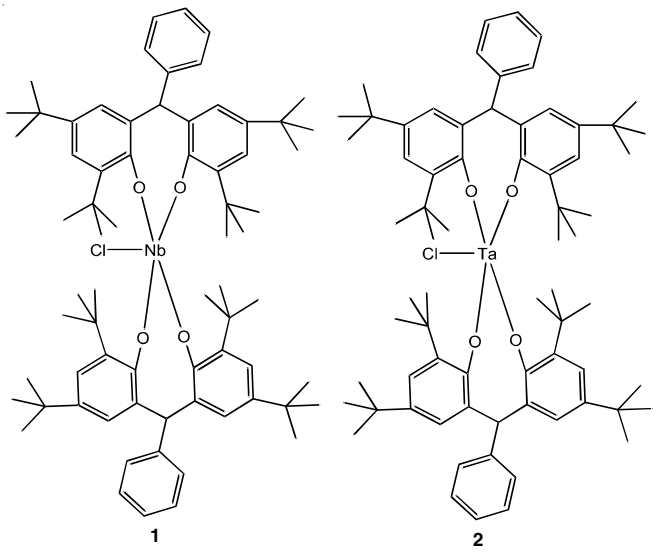
Synthesis of Nb{2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$O]$_2$}$_2$ complex (1): A toluene solution of 20 mL of 2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$OH]$_2$ (1 g, 1.99 mmol) and $NbCl_5$ (1.12 g, 0.99 mmol) was dissolved in 10 mL toluene and mixed with ligand solution. The mixture was refluxed for 6 h followed by the removal of volatiles and extracted the solid into acetonitrile (20 mL) to give red coloured solid complex **1**.

Synthesis of Ta{2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$O]$_2$}$_2$ complex (2): By following same procedure as described for synthesis of complex **1**, the complex **2** was synthesized by the reaction of $TaCl_5$ (1.21g, 0.99 mmol) with 20 mL of 2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$OH]$_2$ (1.00 g, 1.99 mmol) to give pink coloured solid complex **2**.

Ring opening polymerization: Complex **1** or **2** (0.30 g, 266.46 µmol), ε-caprolactone (6.08 mL, 52.39 mmol) and alcohol (0.01 mL, 118.3 µmol) mixed together in absence of solvent and the system was placed in an oil bath at 100 ºC. After 1 h, the mixture quenched by added methanol (250 mL).

RESULTS AND DISCUSSION

The compound 2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$OH]$_2$ was prepared according to reported procedure [4,14] . Reaction of ligand with toluene solution of niobium pentachloride (2:1) ratio and tantalum pentachloride (2:1) ratio has resulted in the formation of Nb{2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$O]$_2$}$_2$ (**1**) complex and Ta{2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$O]$_2$}$_2$ (**2**) complexes.



Structure of Nb{2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$O]$_2$}$_2$ (**1**) and Ta{2,2′-PhCH[4,6-(*t*-Bu)$_2$C$_6$H$_2$O]$_2$}$_2$ (**2**)

Infrared spectra: The IR spectra of both complexes presented a characteristic absorption single at 2900 cm^{-1} belonging to *t*-butyl group while peaks at 3200-3100 cm^{-1} shifted to shorter wave length indicated that coordination has happened through -OH group.

^{1}H NMR spectra: The ^{1}H NMR spectra of complexes was performed in $CDCl_3$ at room temperature. The spectrum of complex **1** revealed the signals at 1.27 (s, 36H, *t*-Bu), 1.30 (s, 36H, *t*-Bu), 3.77 (s, 1H, CH-bridge) and 6.67-7.51 (m, 18H, Ar-H) (Fig. 1). For complex **2**, ^{1}H NMR spectrum showed the signals at 1.29 (s, 18H, *t*-Bu), 1.42 (s, 18H, *t*-Bu), 4.43 (s, 1H, CH bridge) and 7.15-7.43 (m, 18H, Ar-H) (Fig. 2).

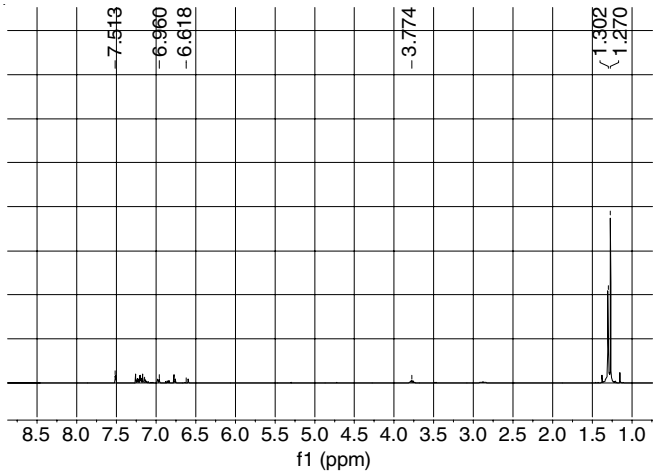


Fig. 1. ^{1}H NMR spectrum of complex **1**

Ring opening polymerization of ε-caprolactone: The ability of synthesized complexes toward the ring opening polymerization of ε-caprolactone were assessed (**Scheme-I**). Polymerization of ε-caprolactone by complexes **1** and **2** which includes the phenoxide group were noted to be active (Table-1). The polymer molecular weight (M_n) obtained by Ta catalyst is much lower as compared to Nb catalyst [16].

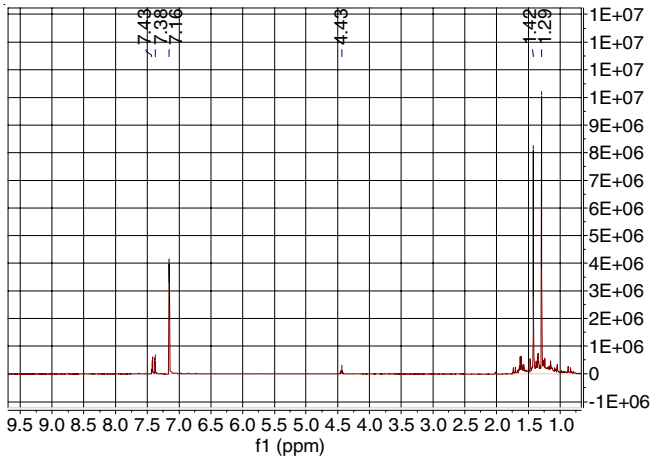
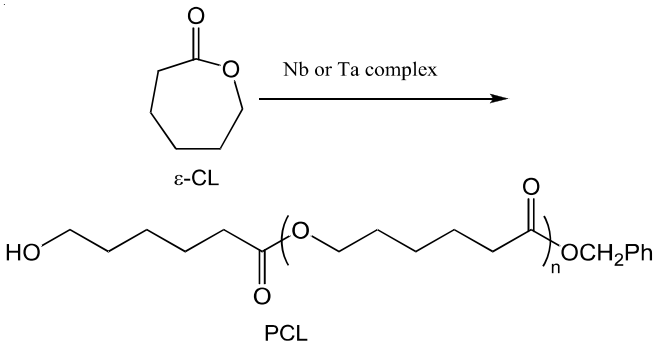


Fig. 2. ^{1}H NMR spectrum of complex **2**



Scheme-I: Ring opening polymerization of ε-CL

TABLE-1
POLYMERIZATION OF ε-CAPROLACTONE USING COMPOUNDS **1** AND **2**[a]

Catalyst	Yield (%)	Time (min)	M_n[b]	PDI[c]
Nb complex	81	30	12900	1.10
Ta complex	77	40	6500	1.29

[a]Conditions: 0.0123 mol of complexes; 1.0 M ε-CL in toluene. CL: [cat] : BnOH = 200:1:1. [b,c]from GPC.

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