Aluminium complexes as catalysts for ring-opening polymerization of ε-caprolactone bearing Schiff base ligands derived from 4,4'-Methylenebis (2,6-diisopropylaniline)

Yahya Al-Khafaji¹, Nour Abd Alrazzak², Suad T. Saad², Ahmed S. Abbas¹ and M Merdan³

¹ Department of Chemistry, College of Science, University of Babylon- Babylon-Iraq
² Department of Chemistry, College of Science for women, University of Babylon- Babylon-Iraq
³ Department of Physics, College of Science, University of Babylon- Babylon-Iraq

Abstract. The mono and binuclear compounds, [4,4’ methylene bis (2,6-diisopropylaniline) (3,5-di-tert-butylsalicylaldehyde)AlEt₂] (1), (2,6-diisopropylaniline)bis-(3,5-tBu₂C₆H₄-O-2)AlEt₂], obtained by reacting between triethyl-aluminium and Schiff base derived from reaction of 4,4' methylene bis (2,6-diisopropylaniline with one and two equivalent of 3,5-Di-tert-butylsalicylaldehyde to form L¹H and L²H₂ respectively. The reaction of L¹H with triethyl aluminium lead to form monometallic complex, while L²H reacted with two equivalent of triethyl aluminium formed bimetallic complex (2). Both ligands and catalysts have been prepared and characterized by IR, ¹HNMR and CHN analysis. The compounds 1 and 2 are investigated as catalysts for the polymerization of ε-caprolactone in the presence of benzyl alcohol. Both complexes showed moderate activity as pre-catalysts for ε-caprolactone polymerisation.

Keywords: Ring opening polymerization (ROP), mono, dimeric Al(III) complexes, 4,4' methylenebis(2,6-diisopropylaniline), ε-caprolactone.

1. Introduction
In recent years, biodegradable polymers attract much interest. This is attributable to the fact that it is environment friendly, renewable and biocompatible [1-3]. It has found various application such as, medical applications as sutures [3] and industry application as packaging materials [4, 5]. Polycaprolactones (PCL) is represented as important biodegradable polymer [6]. It is prepared via polymerization of the ε-caprolactone monomer (CL). Literaturely, coordination chemistry shows a significant role as catalysts toward (ROP) [7]. For examples, complexes based on zinc, [8], lithium, [9] group 6 (Nb and Ta, [10] group 4 vanadium and molybdenum, [11, 12] group (Ι) rare earth metals, [13] that have high ability to polymerize cyclic esters. Organoaluminium complexes have been investigated as catalysts for the ring opening polymerization of cyclic esters. Aluminium complexes as catalysts for the polymerization of cyclic esters are successful initiators [14-16]. Manipulate of Al complexes to be efficient catalysis for ring opening polymerization also, is numerically investigated [17-20]. In addition, Schiff base ligands are easy to prepare [21, 22], when such ligands metal system is used on a large scale. Keeping this in our attention, the employ of Schiff base type ligation has catch the attention of many researchers, and a number of articles have been published concerned above the reasons. There has been attention in the synthesis of di or trimetallic catalysts, depending on cooperative between metals lead to increase catalyst activity. Ma et al has founded the usage of multimetallic aluminium catalyst for the ring opening polymerization of cyclic esters [23]. Essentially they have indicated that it is possible
to induce stereo selectivity with such catalysts in case of lactides polymerization [24]. Recently, we had investigated a series of aluminium complexes derived from Schiff base ligands based on dimethyl amine, methyl phenyl amine and diphenylamine [25]. These complexes showed highly effective initiators in the ring opening polymerization of rac-lactide, L-lactide, ε-caprolactone, etc. little articles have been published on type bi-aluminium Schiff base derived from bisaniline.

2. Experimental:
Under a nitrogen environment all experiments were accomplished by using Schlenk techniques. Dried solvents were used. All chemicals were used as received. Infrared spectra is being recorded via FTIR-8400S SHIMADZU spectrometer. $^1$H NMR analysis was recorded at 300 MHz in a (Bruker) spectrometer. In Abu Ali centre lab-Iran. (C, H, N analyses were completed by the elemental analysis department of chemistry/university of Babylon.

2.1 Synthesis of ligands

In a typical procedure [26], L$^1$H was synthesised via adding ethanol solution of 4,4’-methylenebis(2,6-diisopropylaniline) (3.66 g, 0.01 mol) to ethanol solution of 3,5-di-tert-butylsalicyaldehyde (2.34 g, 0.01 mol). The solution was refluxed for 2 h, after cooling precipitate was formed then was filtered, recrystallized by ethanol yield a yellow solid (4.98 g, 85.5%). Calculated, C 82.34, H 9.94, N 4.80, found: C 82.31, H 9.95, N 4.78. IR= 3109 (bs), 3047 (s), 1603 (s), 1575 (m), 1539 (w), 1489 (s), 1481 (s), 1456 (s), 1456 (s), 1415(s), 1381 (m), 1352 (m), 1305 (m), 1265 (s), 1213 (m), 1151 (m), 1136(m), 1101 (m), 1074 (w), 1045 (m), 1014 (m), 950 (w), 918 (m), 881 (m), 779 (w), 761(m), 750 (w), 702 (s), 680 (s), 663 (w). $^1$H NMR (CDCl3): 9.04 (1H, s, CH=N), 7.55-6.82 (6H, 4S, Ar-H), 5.85 (1H, s, OH), 4.93(2H, s, NH2), 3.88 (2H, sep, CH(CH3)2), 2.45 (2H, sep, CH(CH3)2), 1.55 (9H,s, C(CH3)3), 1.32 (9H,s, C(CH3)3), CH(CH3)2 hiding with C(CH3)3 peaks area.

L$^2$H2 was prepared as for L$^1$H but doubling the number of moles of the 3,5-di-tert-butylsalicyaldehyde (4.68g, 0.02 mol) was added to ethanol solution of amine (4,4’-Methylenebis(2,6-diisopropylaniline)) (3.66 g, 0.01 mol) the solution was refluxed for 3 h, after cooling precipitate was formed then was filtered, recrystallized by ethanol yield an yellow solid (5.23g, 65.45%). calculated. C 82.57, H 9.75, N 3.50 ; found: C 82.55, H 9.72, N 3.23. IR= 3448 (m), 3338 (s), 3113 (w), 2399 (w), 2322 (w), 1630 (s), 1585 (m), 1516 (m), 1495 (s), 1425 (w), 1433 (w), 1390 (m), 1159 (m), 1120 (m), 1065 (m), 1015 (w), 926 (m), 910 (w), 833 (w), 767 (m), 744 (s), 715 (w), 696 (s), 640 (w), 620 (w), 511 (m), 420 (w), 408 (w) cm$^{-1}$. $^1$H NMR (CDCl3): 3.85 (2H, s, CH=H), 8.03-6.94 (8H, 6S, Ar-H), 5.73(2H, s, OH), 3.85 (2H, s, CH2), 2.16 (4H, sep, CH(CH3)2), 1.33 (18H,s, C(CH3)3), 1.29 (18H,s, C(CH3)3), 0.96-0.85 (24H, 2d, CH(CH3)2).

2.2 Synthesis of complexes [27]

2.2.1. Synthesis of [4,4’ methylenebis(2,6-diisopropylaniline) (3,5-di-tert-butylsalicyaldehyde)AlEt3] (I): A toluene solution of AlEt3 (1.40 mL, 0.0028 mol, 2 M in toluene) was added to (75 mL) of toluene solution of L$^1$H (1.16, 0.002 mol). The mixture was refluxed for 3h, the resulting solution was cooled to room temperature, then by vacue the volatiles were removed to form yellow solid which recrystallized by acetonitrile to give I. Yield 0.64 g, 55.17 %. IR (Nujol mull, KBr)= 3449 (m), 3335 (s), 3194 (w), 3107 (w), 2399 (w), 2322 (w), 1630 (s), 1585 (m), 1516 (m), 1495 (m), 1423 (m), 1387 (m), 1332 (m), 1257 (m), 1238 (w), 1124 (m), 1063 (w), 1058 (w), 920 (w), 833 (m), 744 (w), 712 (w), 637 (w), 573 (w), 513 (m) cm$^{-1}$. 
2.2.2. Synthesis of [4,4′ methylenebis(2,6-diisopropylaniline)bis- (3,5-di-tert-butylsalicylaldehyde)AlEt2] (2)
As for 1, except using L2H2 (1.59 g, 0.002 mol) and AlEt3 (2.4 mL, 0.0048 mmol, 2 M in toluene), giving 2. IR= 2953 (s), 2909 (w), 2868 (w), 1647 (s), 1586 (m), 1553 (m), 148 (m), 1382 (m), 1314 (m), 1276 (m), 1251 (m), 1230 (w), 1205 (w), 1190 (m), 1171 (m), 1163 (w), 1110 (s), 1040 (w), 1027 (w), 970 (w), 950 (w), 878 (m), 855 (m), 785 (m), 768 (w), 668 (w), 533 (w), 410 (w) cm−1. 1H NMR (CDCl3): 8.99 (2H, s, CH=N), 8.64-6.81 (8H, m, Ar-H), 3.95 (2H, s, CH2), 3.10 (4H, sep, CH(CH3)2, 1.56 (18H, s, C(CH)3), 1.31 (18H, s, C(CH)3), 0.99 (24H, m, CH(CH3)2)–0.33 (m, 8 H, Al(CH2CH3)2 ppm.

3. Results and discussion
3.1. Synthesis of the ligand (E)-2-(((4-(4-amino-3,5-diisopropylbenzyl)-2,6 diisoproplyphenyl) imino)methyl)-4,6-di-tert-butylphenol (L1H) and 6,6′-((1E,1′E)-((methylenebis(2,6-diisopropyl-4,1 phenylene)) bis(azaneylylidene)) bis(methaneylylidene)) bis(2,4-di-tert butylphenol) (L2H2)
The compound (E)-2-(((4-(4-amino-3,5-diisopropylbenzyl)-2,6 diisoproplyphenyl) imino)methyl)-4,6-di-tert-butylphenol (L1H) and the compound 6,6′-((1E,1′E)-((methylenebis(2,6-diisopropyl-4,1-phenylene)) bis(azaneylylidene)) bis(methaneylylidene)) bis(2,4-di-tert butylphenol)(L2H2) were prepared in good yield (85.5 %) and (65.45) respectively via reacting the compound 4,4′-methylenebis(2,6-diisopropylaniline) with one equivalent of the compound 3,5-di-tert-butyl-2-hydroxybenzaldehyde in case of L1H and two equivalent in case of L2H2 in absolute ethanol (Scheme 1). The presence of azomethine bond in first ligand and second one is proved by the presence of a signal in their 1H NMR (9.04 and 8.35) (Figure 1 and 2) whereas in their IR spectra, the signal belong to the azomethine bond appears at 1575 cm−1 (L1H), and 1585 cm−1 (L2H2). A search of the Reaxys showed 0 result for the bianiline with 3 5-di-tert-butylsalicylaldehyde Schiff base.

3.2 Preparation of complexes.
The interaction of pro-ligands L1H and L2H2 with AlEt3 in a 1:1 and 1:2 equivalents ratio in toluene with reflux produced the monometallic aluminium ethyl complex (1) and bimetallic aluminium ethyl complex (2) respectively both pale yellow solids after recrystallization by n-hexane (Scheme 1). The resulting compounds were characterized by 1H and IR spectra. The proton nuclear magnitude resonance spectra of the complexes 2 reveal signal below zero belong to aluminium carbon bond at –0.33 (Figure 3). In addition absence of hydroxyl signal on both aromatic ring which appear around 5.7 ppm further evidence to form a complex(2), there is no clear HNMR for complex(1) observed from experiments. But there is a clear IR signal peak at 1575 cm−1.

3.3. Polymerization of ε-caprolactone.
Polymerization of ε-CL was studied by adding of benzyl alcohol (1.0 equiv. to aluminium complexes), the results are mentioned in (Table 1). At a ε-CL/Cat molar ratio of 200, the catalyst 2/ BnOH system produced high molecular weight of polycaprolactone, the yield percentage closely to 98 % after 1 h (entries 3–6). Linearity was noted between the mole ratio and the (Mn) values with acceptable molecular weight distribution (Figure 4). Complex 1 activity as compared with complex 2 was higher and narrow PDI (≤1.29), revealed that, the presence of the bimetallic system in 2 is advantageous in terms of yield percent and
molecular weight distribution (runs 1 versus 2) [28-30]. According to runs 3 to 6, there was a linear relation between the average molecular weight ($M_n$) and $[\varepsilon$-CL]/[2] (Figure 4). Also, the linear relationship between average molecular weight versus monomer mole ratios ([$\varepsilon$-CL]/[2]) suggested that a living process. Runs 3-6 revelled that the observed ($M_n$) increase with the increasing of the ($\varepsilon$-Cl: Al) for complex 2 from 50: 1 to 200: 1 with the increasing of the yield percent from (91 to 98)% whereas PDI remains constant (1.24–1.29).

Scheme 1: Ligands and complexes used in this paper

Figure (1). The $^1$HNMR spectrum of ligand(L$^1$H).
Figure (2). $^1$HNMR of the ligand (L$^2$H$_2$).

Figure (3). $^1$HNMR of the complex (2).

Table 1. Results of polymerization of (ε-CL) catalyzed by complexes 1 and 2.

| Run | Cat | T (°C) | CL : M :BnOH | Yield$^a$ (%) | $M_n$ ,GPC | PDI$^d$ |
|-----|-----|--------|---------------|--------------|------------|--------|
| 1   | 1   | 30     | 200 : 1:1     | 63           | 3040       | 1.13   |
| 2   | 2   | 30     | 200 : 1:1     | 74           | 3780       | 1.17   |
| 3   | 2   | 60     | 50 : 1:1      | 91           | 7820       | 1.24   |
| 4   | 2   | 60     | 100 : 1:1     | 91           | 10040      | 1.28   |
| 5   | 2   | 60     | 150 : 1:1     | 92           | 15390      | 1.18   |
| 6   | 2   | 60     | 200 : 1:1     | 98           | 23970      | 1.29   |
Experiments accomplished in toluene using 0.051 mmol of aluminium complexes; 10 mmol of \(\varepsilon\)-caprolactone, \(\text{b} M_n\) from (GPC) values corrected by using with correction factors 0.56. \(\text{d}\) From GPC.

![Graph](image)

**Figure (4). The relationship between average molecular weight and the [CL]/[2].**

4. **Conclusions**

In conclusion, new complexes of aluminium (III) complexes have been synthesized, characterized and studied catalytic behaviour of these complexes for the polymerization of (\(\varepsilon\)-CL) by ROP process. Control manner was observed for the ring opening polymerization in terms of PDI and average molecular weight. The polymerization procedure using aluminium complexes as catalysts required add benzyl alcohol as an initiator. Structure activity relationship was observed, for instance, it was advantageous to use the bimetallic system in term of high \( M_n \) value and narrow PDI.

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