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New Nickel and Copper Complexes With Thiacalix[4]Arene Derivative Synthesis, Characterization and Catalytic Activity

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Abstract: *The study investigates the synthesis and characterization of p-tert-butylthiacalix[4]arene derivative via interaction between p-tert-butylthiacalix[4]arene with two equivalent of 1-bromopropyl to form di-substituted thiacalix[4]arene ring. It is employed to prepare complexes with Ni(II) and Cu(II). The ligand and it is complexes were characterized using elemental analysis, infrared and proton nuclear resonance. Polymerization of cyclic esters was assisted via prepared complexes. The result shows capability of these compounds as catalyst for such reaction.*

Keywords: *Ring Opening Polymerization, thiacalix[4]arene, Bromopropyl, Ni(II) and Cu(II).*

Introduction

The architectures of new ligand in the coordination chemistry is a field of more interes (Fisher et al, 2004) (Malinowski, J et al, 2020), A serious of articles have been well prepared to employ in different field (Benesperi et al, 2006) (Angell et al, 2006) (Al-khafaji, 2023) (Ismail et al, 2020). One of the vital application of coordination compounds are there ability for ring opening polymerization of biode (Ulery et al, 2011) (Daniel, 2011) gradable monomer (Al-khafaji, 2023) (Al-khafaji, 2017) (Ge, F et al, 2016). The production of biodegradable polymer catch more attention owing the fact that their variety of application (Hussein et al, 2021) for example, medical application (Ulery et al, 2011) (Daniel, 2011) water purification (Chopparapu, R et al, 2020) (Samir, A, et al, 2022), agriculture (Maraveas, C,

2020) (Kiselev et al, 2021). Ring opening polymerization one of the important procedure that employed to prepare biodegradable polymer via polymerization of bio-monomer (Naumann, S et al, 2015) such as e-caprolactone (Von Schenck, 2002).

Literraturely, metals complexes shows high ability toward ROP of lactone. Such examples, of using complexes as catalysts are based on lithium, zinc (Al-khafaji, 2017), (Nb (Al-khafaji, 2018). Large molecules complexes such as thiacalixarene also, was studied to promote ROP of biodegradable monomers (Kim, K, 2011) (Shurpik, 2018). In this study thaicalix[4]aren derivative complexes of nickel and copper ion were synthesized and characterized with p-tert-butylthiaclix[4]aren derivative.

Experimental

Preparation of trispropoxy-p-tert-butylthiacalix[4]arene

A round bottom flask was charged with a mixture of barium hydroxide (1.19 g,7 mmol) and p-tertbutylthiacalix[4]arene(1.44g, 2 mmol) in (25 mL) DMF fellow by stirring the mixture for 1 hour at r.t. Fellow by slowly adding 1-bromopropane (4.91 g, 40 mmol) the and the mixture stirring at r.t. for (4 h) . Dichlorometane was used to extracted the suspension then, 50 mL water was employed to wash the resulting compound. Anhydrous sodium sulfate was added to dried the organic phase the organic solution was evaporated to form a white solid (CH_3OH/CH_2Cl_2). The yield was 70%. Calcd.: C, 68.62; H, 7.51, found C, 69.05; H, 7.77, IR: 3370 (s), 3120 (m), 1649 (m), 1590 (w), 1450 (s), 1420 (m), 1378 (m), 1306 (m), 1245 (w), 1088 (m), 760 (s), 685 (m), 570 (s); ^{1}H NMR ($CDCl_3$): δ 1.56(***t-Bu***, s, 36 H), 1.97(C_2H_5-***CH_3***, t, 6 H), 2.61(-O***CH_2***-CH_2CH_3, t, 4H), 3.59 and 4.31 (CH_2-***CH_2***-CH_3, m, 2H, each), (6.49- 7.19 (,***Ar-H***, m, 8H). 9.82 (***Ar-OH***, s, 2H)

Synthesis of trispropoxy-ptert-butylthiacalix[4]arene complex

Synthesis of nickel complex(1)

An ethanol solution (20 mL)of Dipropoxy-*p*-tert-butythialcalix[4]arene (0.40g,0.5 mmol), fellow by adding nickel nitrite hexahydrate(0.14 g, 0.5 mmol) the mixture was stirred and heated to temperature around 70 °C for (2 hours). Then the mixture was allowed to cool, the product was formed and collected. A green powder of nickel complex were formed in yield 63%. Calcd.: C, 64.10; H, 6.78 found C, 65.01; H, 6.89 IR: 3290 (s), 3140 (m), 1655 (s), 1590 (s), 1452 (s), 1422 (m), 1370 (m), 1301(m), 1246 (w), 1076 (m), 760 (s), 686 (m), 572 (s).), 480 (s). ^{1}H NMR ($CDCl_3$): δ 1.54(***t-Bu***, s, 36 H), 2.35(C_2H_5-***CH_3***, t, 6 H), 2.93(-O***CH_2***-CH_2CH_3, t, 4H), 3.16 (CH_2-***CH_2***-CH_3, m, 2H), 7.21- 7.62 (,***Ar-H***, m, 8H).

Synthesis of cooper complex(1)

Same for complex (1) but using copper nitrite trihydrate (0.12 g, 0.5 mmol) the mixture was stirred and heated to temperature around 70 °C for (2 hours). Then the mixture was allowed to cool, the product was formed and collected. A light blue powder of copper complex were formed in yield 55%. Elemental analysis: C, 63.74; H, 6.75 found C, 63.01; H, 6.65 IR: 3290 (s), 3144 (s), 1653 (m), 1590 (s), 1444 (m), 1428 (w), 1370 (m), 1307(m), 1244 (s), 1077 (s), 770 (s), 645 (m), 565 (s), 530 (s), 490 (w) . ^{1}H NMR ($CDCl_3$): δ 1.18(***t-Bu***, s, 36 H), 2.04(C_2H_5-$\boldsymbol{CH_3}$, t, 6 H), 2.79(-O$\boldsymbol{CH_2}$-CH_2CH_3, t, 4H), 2.96 (CH_2-$\boldsymbol{CH_2}$-CH_3, m, 2H), 7.62- 7.92 (,***Ar-H***, m, 8H).

Application as ring opening polymerization catalysts

The procedure done by adding benzylalcohol (1 equivalent) to the solution of e-caprolactone(2.5 mmol) fellow by adding the solution of complex 1 and 2. The mixture was stirred for 1 hour then the mixture quenched by methanol, fellow by collecting and drying the precipitate.

Methodology

Synthesis of Ligand and Complexes

1. Preparation of trispropoxy-p-tert-butylthiacalix[4]arene:

The ligand was synthesized by reacting barium hydroxide with p-tert-butylthiacalix[4]arene in DMF, followed by the addition of 1-bromopropane. The reaction mixture was stirred at room temperature for 4 hours. The product was isolated by extraction with dichloromethane and washing with water, followed by drying with anhydrous sodium sulfate. The yield was 70%.

2. Synthesis of Nickel Complex (Complex 1):

The nickel complex was prepared by reacting dipropoxy-p-tert-butylthiacalix[4]arene with nickel nitrite hexahydrate in ethanol. The reaction mixture was heated to 70°C for 2 hours, then allowed to cool. The resulting green powder of nickel complex was obtained with a yield of 63%.

3. Synthesis of Copper Complex (Complex 2):

A similar procedure was followed using copper nitrite trihydrate instead of nickel salt, yielding a light blue powder with 55% yield.

Characterization Techniques

- Elemental analysis was conducted to confirm the chemical composition of the synthesized compounds.
- Infrared (IR) spectroscopy and proton nuclear magnetic resonance (^1H NMR) spectroscopy were employed to identify functional groups and confirm structural features.
- The absence of hydroxyl group stretching bands in the IR spectra and the disappearance of specific proton signals in the ^1H NMR spectra indicated successful complexation.

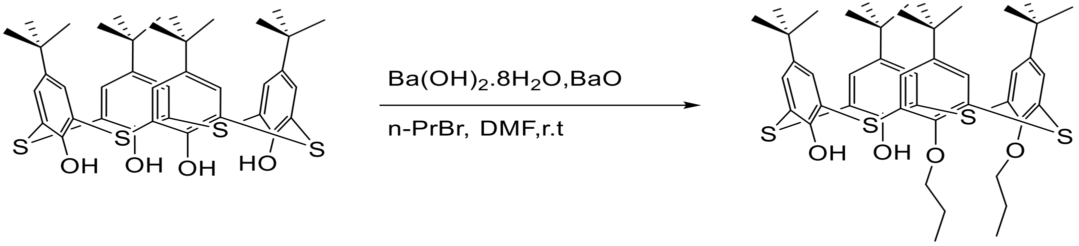
Catalytic Activity Study

Ring-opening polymerization (ROP) of ε-caprolactone was performed using complexes 1 and 2 as catalysts. The reactions were conducted at room temperature and 110°C. Benzyl alcohol was used as an initiator, and methanol was employed to quench the reaction. The polymerization products were collected and analyzed.

Result and Dicscussion

Preparation of the ligand

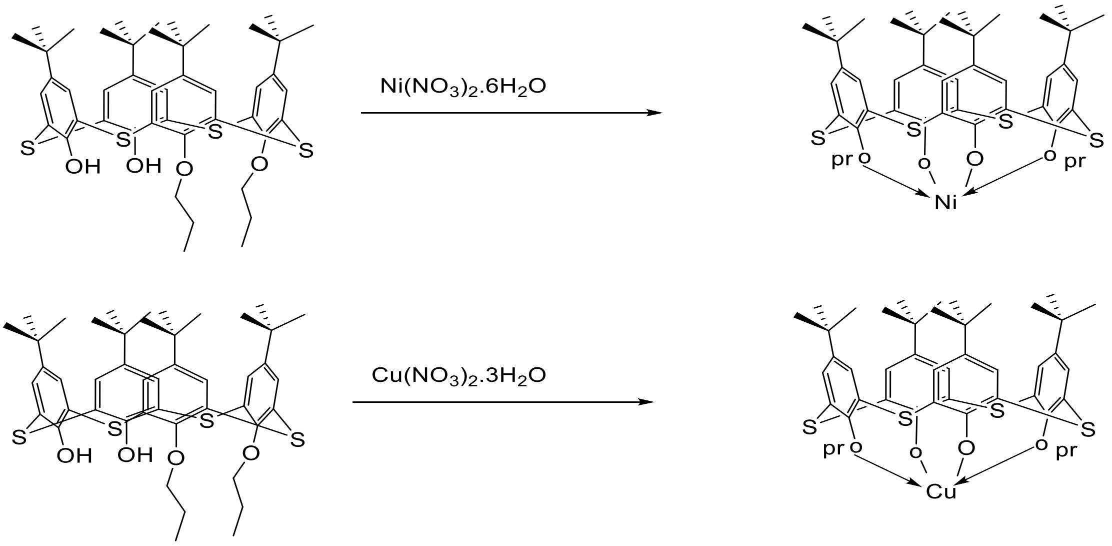
Interaction two equivalent of 1-bromopropane with p-tert-butylthiacalix[4]arene gave the di-propoxy thiacalix[4]arene Scheme(1), in infra-red spectrum the hydroxyl appear at (3350 cm^{-1}) also, in the ^{1}HNMR spectrum prove all characteristic group Figure 1.



Scheme 1. Preparation of dipropoxy-p-tert-butylcalix[4]arene

Preparation of complexes (1) and (2)

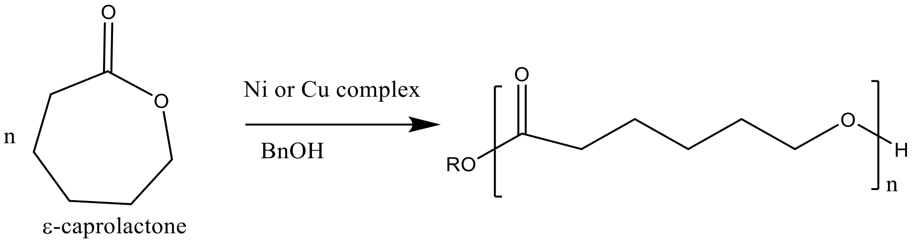
Interaction of prepared ligand with 1 equivalent of nickel nitrite hexahydrate and copper nitrite trihydrate afforded, powder with monometallic complex Scheme(2). For both complexes, the ^{1}HNMR spectra was found in deuterated chloroform . The signal at around 10 ppm in the ^{1}H NMR spectra of the ligand belong to Ar-OH was absented in the proton nuclear resonance spectra of the prepared complexes, while all other the peak of characteristic protons were slightly shifted in the spectra Figure 2 and Figure 3. In addition, absence the band around 3300 cm^{-1} assigned to the hydroxyl group stretching in complexes spectrum,



Scheme 2. Preparation of complexes

Polymerization of ⚜-caprolactone

The nickel and copper complexes **1** and **2** were studied for ROP of ⊚-CL Scheme 3. was found from the table 1. it seem to be the catalysts active at room temperature and high temperature(110 °C). At high temperature the copper complex **was** high active than nickel complex also the conversions was high. The polydispersities were narrow for all produced molecular weight.



Schem 3. Polymerization of ◎-caprolactone

Table 1. Polymerization of ε-CL via catalysts 1 and 2

Complexes	T/°C	Conv.%	*Mn*	PDI
Complex- 1	r.t	40	2864	1.233
Complex-2	r.t	44	3134	1.174
Complex-2	110	77	4399	1.171

Caprolactone: complex :BnOH= 200:1:1

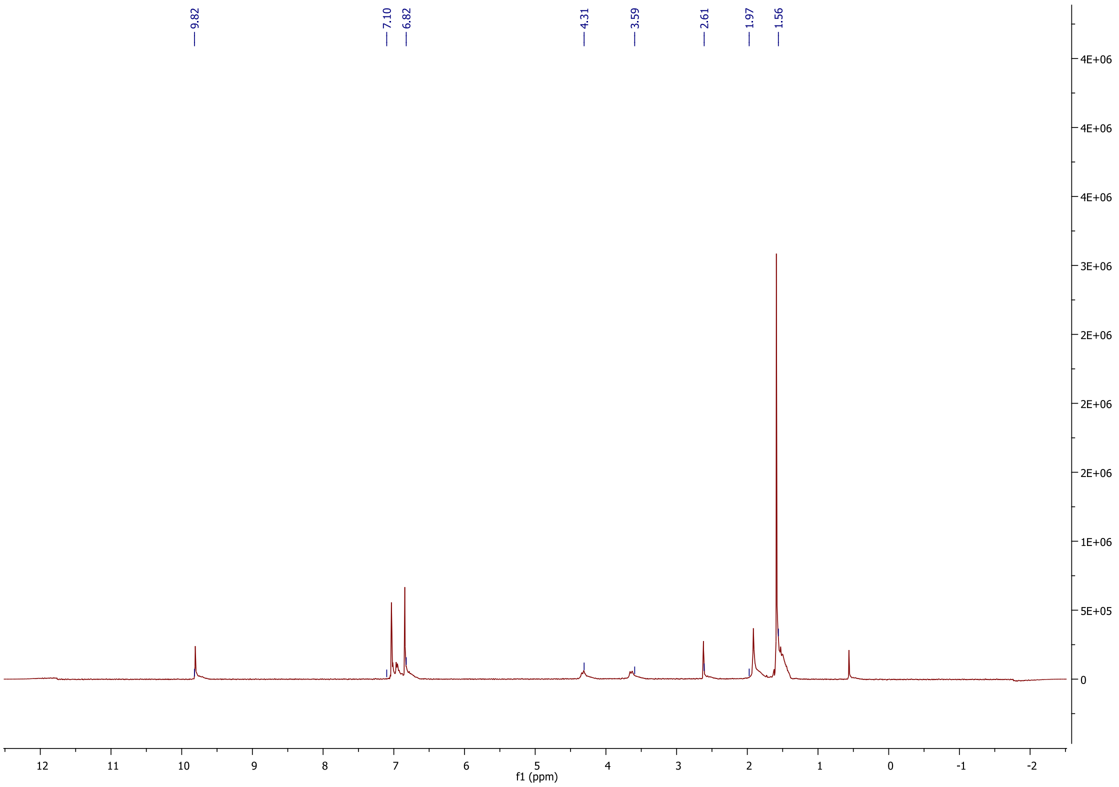


Figure 1. ^{1}HNMR for the ligand

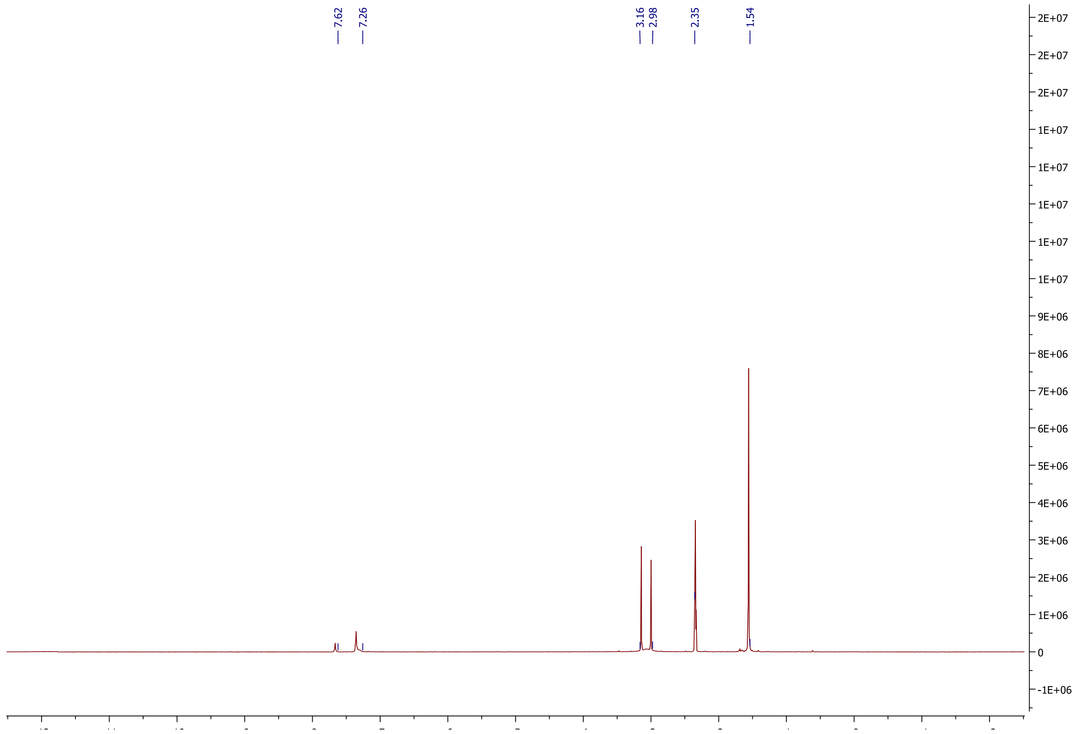


Figure 2. ^{1}HNMR for Ni complex

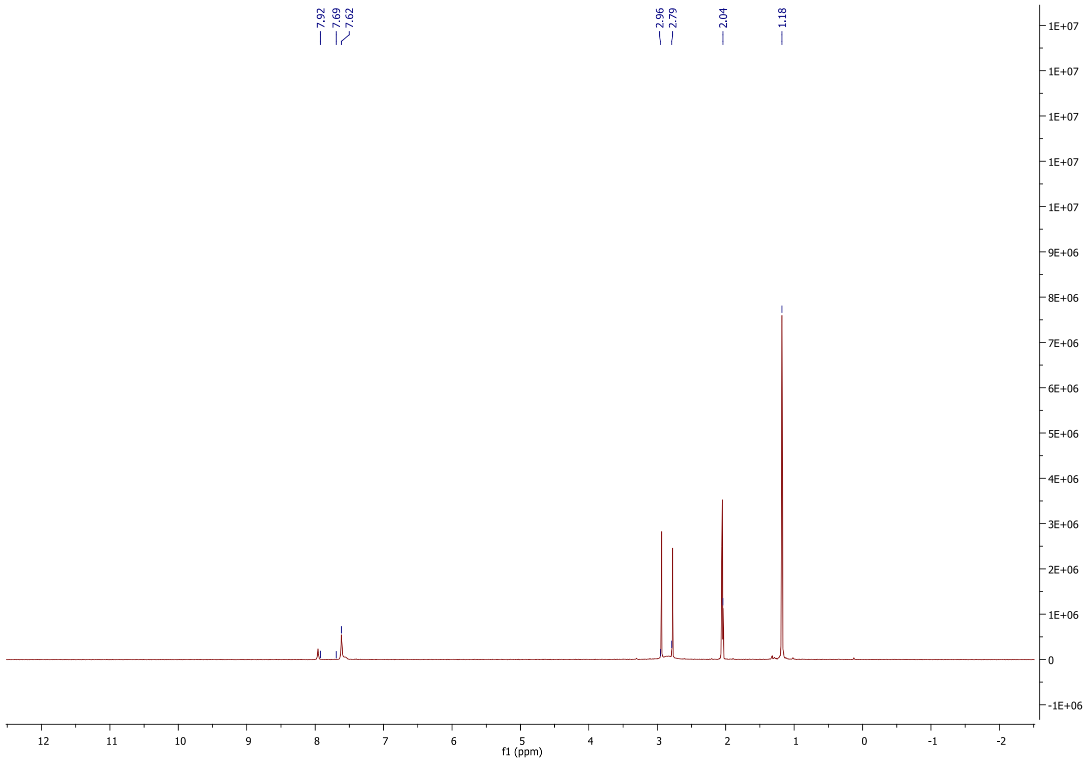
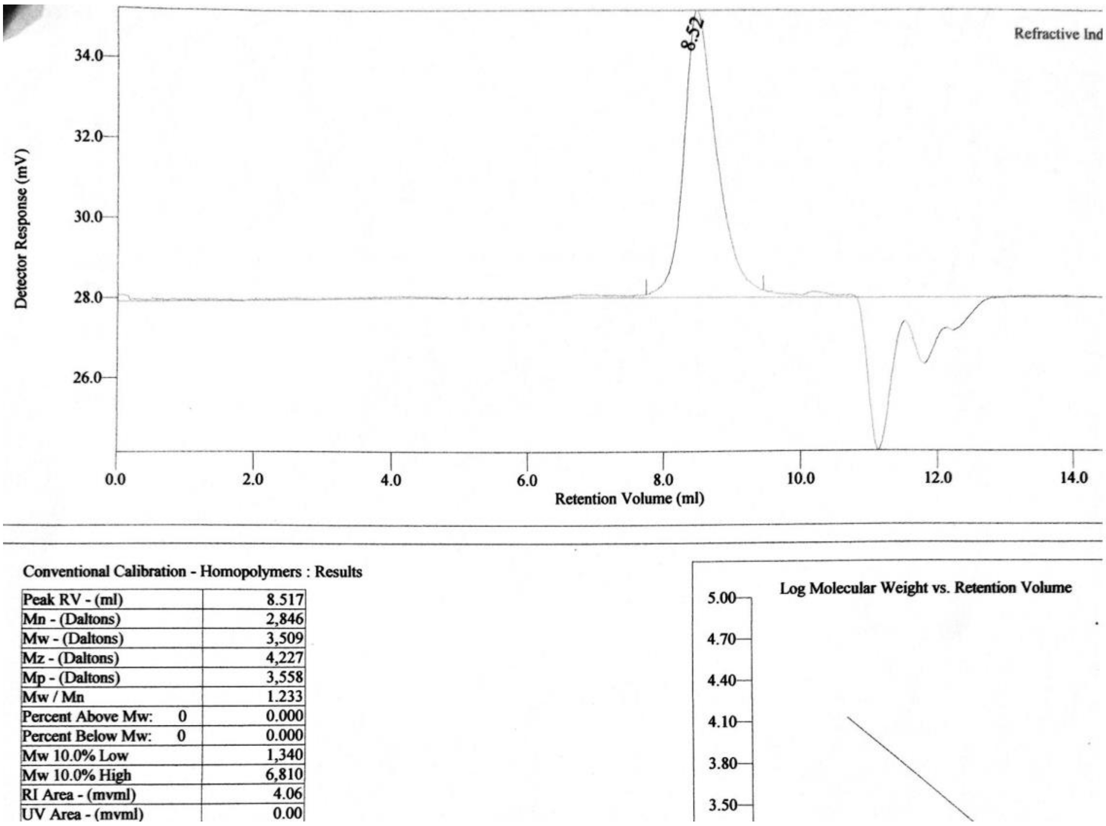


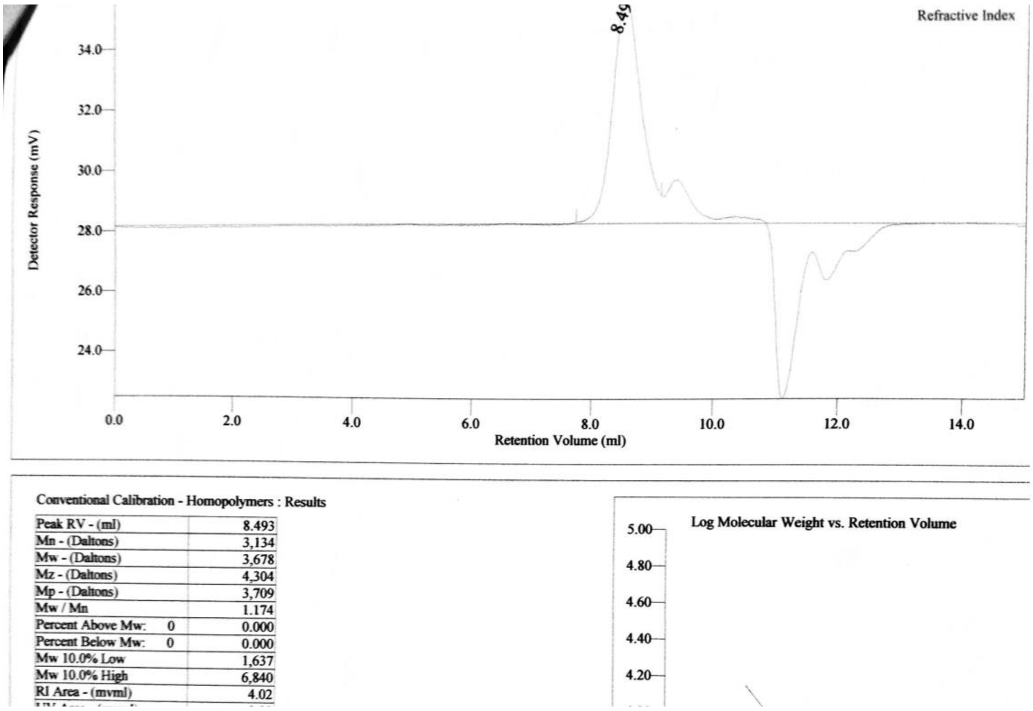
Figure 3. ^{1}HNMR for Cu complex



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8.517
Mn - (Daltons)	2,846
Mw - (Daltons)	3,509
Mz - (Daltons)	4,227
Mp - (Daltons)	3,558
Mw / Mn	1.233
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	1,340
Mw 10.0% High	6,810
RI Area - (mvml)	4.06
UV Area - (mvml)	0.00

Figure 4. Gpc for polymerization of caprolactone by Ni complex



Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	8.493
Mn - (Daltons)	3,134
Mw - (Daltons)	3,678
Mz - (Daltons)	4,304
Mp - (Daltons)	3,709
Mw / Mn	1.174
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	1,637
Mw 10.0% High	6,840
RI Area - (mvml)	4.02

Figure 5. Gpc for polymerization of caprolactone by Cu complex

Conclusion

This study successfully synthesized and characterized new nickel and copper complexes of dipropoxy-p-tert-butylthiacalix[4]arene. The complexes were shown to be effective catalysts for the ring-opening polymerization of ε-caprolactone. At room temperature, both catalysts exhibited moderate activity, with copper complex showing slightly higher conversion. At elevated temperature (110°C), copper complex demonstrated superior catalytic performance, achieving higher conversion and narrower polydispersity. These findings suggest the potential application of thiacalixarene-based metal complexes as efficient catalysts for the preparation of biodegradable polymers. Further studies on optimizing reaction conditions and exploring other monomers are recommended.

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