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Preparation And Characterization Of Calixarene Derivative Complexes And Their Application As Catalysis For Ring Opening Polymerization Of ε-Caprolactone.

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Abstract

Tripropoxy-*p-tert*-butylcalix[4]arene and tripentoxy-*p-tert*-butylcalix[4]arene and their complexes with chromium, cobalt and niobium were synthesized. New compounds were characterized by infrared and nuclear megnatic resonance. All complexes were monometallic system. The ability of the complexes toward polymerization of □-caprolactone was investigated by ring opening polymerization mode. One can conclude that the complexes showed modrate activity in term of average molecular weight (M_n) with narrow polydispersity(PDI) and good yield percentage.

Keywords: tripentoxy-*p-tert*-butylcalix[4]arene; niobium; cobalt; chromium; ε-caprolactone.

1. Introduction

A large number of reported articles about metals-based for polymerization systems by ring opening polymerization (ROP) since the important work by Luechs[1]. A variety of ligand systems were employed such as Schiff bases,[2] di or tetra-phenolates,[3] whilst the use of the other ligand system such as calixarene-based system for the ring opening polymerization has received little attention specially for cyclic esters.

The use of calix[*n*]arenes catch more attentions in catalytic/polymerization system owing the fact that calix[n]arenes have advantageous features such as separation procedures[4], biological applications[5], ability to bind with different ionic and natural species[6], also important feature for calix[n]arene is application in supramolecular as (nanotubes[7], capsules[8]. More attention is given during the past few decades to calix[n]arene derivatives and their complexes, many examples of such compounds with first group[9], second group[10, 11] and transition metals (block d)[12, 13]. Up to the present time, several calixarenes complexes that possess metals were reported. Few examples of them described as catalysts for ring opening polymerization of cyclic esters[14, 15].

The present work aim to describe the use of p-tert-calix[4]arene derivitve ligand for the synthesis of a new Chromium(III), Cobalt(II) and Niobium(**V**) complexes and investigate their ability as catalysts for ring opening polymerization of ε-caprolactone.

2. Experimental

2.1 General

By employing Schlenk techniques all experiments were carried out under inert gas. ^{1}HNMR data were recorded at 300 MHz in a (Bruker) spectrometer, in

Abu Ali centre lab-Iran. Melting points were recorded an a SMP30, Strut England. IR spectra is carried out via FTIR-8400S SHIMADZU spectrometer, department of chemistry the university of Babylon.

2.2. Synthesis of 25, 26, 27-tripropoxy- 28-hydroxy *p-tert*-butyl-calix[4]arene (L^1H_1) and their complexes.

2.2.1. Synthesis of 25, 26, 27-tripropoxy- 28-hydroxy p-tert-butyl-calix[4]arene L^1H_1 By flowing Shinkai procedure[16].

2.2.2. Synthesis of {p-t-Bu-calix[4]- (O-Pr)₃}Cr(NO₃)₂ (1)

L^1H_1 (0.5 g, 0.64 mmol) was dissolved in toluene (20 mL). $Cr(NO_3)_3$ (0.16 g, 0.64 mmol) was added and the mixture was heated under refluxed for 3h. Then the volatiles were dried in *vacuo* and recrystalyzed by acetonitrile, fellow by drying in vacuo to form green. (0.41 g, 67 %). M.p(230 ºC). IR: 3171m, 2958m, 1707m, 1604w, 1481m, 1457s, 1375w, 1363m, 1290m, 1255m, 1201s, 1033w, 869s, 810s, 783s, 721m, 675m, 592m, 460w, 430w. ¹HNMR (CDCl₃ at room temperature): δ 0.82(s, C(CH₃)₃,18H), 0.93(t,-CH₂CH₂CH₃, 6H),1.01(s, C(CH₃)₃,9H), 1.07 (t,-CH₂CH₂CH₃, 3H), 1.26(s, C(CH₃)₃, 9H), 1.83-1.91(m, CH₂CH₂CH₃, 4H), 1.97-2.05 (m, CH₂CH₂-CH₃, 2H), 3.18(d, ArCH₂Ar, 2H) 3.25(d, ArCH₂Ar, 2H), 3.29 (d, ArCH₂Ar, 2H), 3.84 (d, ArCH₂Ar, 2 H), 3.78(t, OCH₂, 4H), 3.93 (t, OCH₂, 2H), 6.49(d, Ar-H, 2H), 6.87(s, Ar-H, 2H), 7.04(d, Ar-H, 2H) and 7.12 (s, Ar-H, 2H).

2.2.3. Synthesis of {p-t-Bu-calix[4]- (O-Pr)₃}CoCl (2)

As for (1) but using $CoCl_2$ (0.10 g, 0.64 mmol) purple powder formed(0.33g, 55%). M.p(290 ºC). IR: 3147 w, 2958 s, 2868. m, 2360 m, 1651 w, 1600 w 1537 w, 1483 s, 1464 m, 1365 s, 1294 m, 1247 w, 1201 s, 1114 w, 873 m, 725 m, 461 w, 430 w. ¹HNMR (CDCl₃ at room temperature): δ 0.81(s, C(CH₃)₃,18H), 0.94(t,-CH₂CH₂CH₃, 6H), 1.00(s, C(CH₃)₃,9H), 1.07 (t,-CH₂CH₂CH₃,3H), 1.26(s,C(CH₃)₃, 9H),1.84-1.91(m,CH₂CH₂-CH₃, 4H),1.98-2.08(m,CH₂CH₂-CH₃, 2H),3.17(d, ArCH₂Ar, 2H), 3.19(d, ArCH₂Ar, 2H), 3.24(d, ArCH₂Ar, 2H) 3.78 (d, ArCH₂Ar, 2H), 3.75(t, OCH₂, 4H), 3.83(t, OCH₂, 2H), 6.51(d, Ar-H, 2H), 6.86(s, Ar-H, 2H), 7.03(d, Ar-H, 2H), 7.14 (s, Ar-H, 2H).

2.2.4. Synthesis of {p-t-Bu-calix[4]- (O-Pr)₃}NbCl₄ (3)

As for (1) but using $NbCl_5$ (0.10 g, 0.64 mmol) red powder formed (0.30g, 46 %). M.p(310 ºC) IR: 3149 s, 3059 w, 3028 w, 2958 s, 2906 w, 2868 w, 2335 m, 1606 m, 1481 s, 1386 s, 1303 m, 1201 s, 869 s, 817 s, 783 s, 704 m, 596 w, 524 w, 434 w. ¹HNMR (CDCl₃ at room temperature): δ 0.82(s, C(CH₃)₃,18H), 0.95 (t,-CH₂CH₂CH₃, 6H), 1.00(s, C(CH₃)₃,9H), 1.32(s, C(CH₃)₃, 9H),1.11 (t,-CH₂CH₂CH₃,3H),1.79-1.85(m, CH₂CH₂-CH₃, 4H),1.97-2.08 (m, CH₂CH₂-CH₃, 2H), 3.14(d, ArCH₂Ar, 2H), 3.20(d, ArCH₂Ar, 2H), 3.29 (d, ArCH₂Ar, 2H), 3.96 (d, ArCH₂Ar, 2H), 3.75 (t, OCH₂, 4H), 3.83(t, OCH₂, 2H), 6.52(d, Ar-H, 2H), 6.85(s, Ar-H, 2H), 7.06(d, Ar-H, 2H), 7.15 (s, Ar-H, 2H).

2.3. Synthesis of 25, 26, 27-tripentoxy- 28-hydroxy *p-tert*-butylcalix[4]arene (L^2H_1) and their complexes.

2.3.1. Synthesis of 25, 26, 27-tripentoxy- 28-hydroxy p-tert-butylcalix[4]arene L^2H_1

In a 250 ml round-bottomed flask were placed (1.30 g, 2.00 mmol) of *p-tert*-butylcalix[4]arene and (2.21g, 7.00 mmol) of $Ba(OH)_2.8H_2O$ in DMF (35 mL). This mixture stirred at room temperature for half hour under nitrogen atmosphere. Then (11.88 g, 60 mmol) of 1-Iodo-pentane was added dropwise and the mixture will be further strired at room temperature for 4 hours. Then the suspension was extracted with (100 mL) CH_2Cl_2 and washed with water (2*50 mL). The organic layer will be dried with anhydrous Na_2SO_4 and evaporated by rotary evaporator to afford a white solid. The product will be purified by recrystallization (methanol/CH_2Cl_2) 10:3 v/v. White powder formed(0.72 g, 62 %). M.p(210-212) ºC. IR: 3398 m, 2958 s, 2704 s, 2474 w, 1479 w, 1383 s, 985 m, 825 m, 520 w. ¹HNMR (CDCl₃ at room temperature): δ 0.82(s, C(CH₃)₃,18H), 0.92 (t,-CH₂CH₂CH₂CH₃, 6H), 0.95(m, -CH₂CH₂CH₂CH₂CH₃, 12H), 1.32(s, C(CH₃)₃, 9H),1.55(s, C(CH₃)₃, 9H), 1.42 (t,-CH₂CH₂CH₂CH₂CH₃, 6H),1.82-1.98(m,-CH₂CH₂CH₂CH₂CH₃,4H)+(t,-CH₂CH₂CH₂CH₂CH₃,3H),2.26-2.32(m, CH₂CH₂CH₂CH₂CH₃, 2H), 3.15(d, ArCH₂Ar, 2H), 3.22(d, ArCH₂Ar, 2H), 3.23(d, ArCH₂Ar, 2H),

4.38(d, ArCH_2Ar, 2H) , 3.79 (t, OCH_2, 4H), 3.90 (t, OCH_2, 2H), 5.73 (s, Ar-OH,1H), 6.51(d, Ar-H, 2H), 7.07(s, Ar-H, 2H), 7.12(d, Ar-H, 2H), 7.25 (s, Ar-H, 2H).

2.3.2 Synthesis of {*p-t*-Bu-calix[4]- (*O*-Pen)$_3$}Cr(NO$_3$)$_2$ (4)

L^{2}H$_1$ (0.5 g, 0.61 mmol) was dissolved in toluene (20 mL). Cr(NO$_3$)$_3$ (0.14 g, 0.61 mmol) was added and the mixture was heated under refluxed for 2h. Then the solution was dried and recrystalyzed by acetonitrile, fellow by drying in vacuo to form dark green. (0.42 g, 70 %). M.p(250 ℃). IR: 3109 w, 2958 s, 2866 w, 1726 s, 1700 w, 1680 w, 1483 s, 1405 w, 1310 w, 1290 s, 1203 s, 1185 w, 1130 m, 1037 m, 873 m, 804 m, 723 w, 520 w, 466 m, 440 w. ^{1}HNMR (CDCl$_3$ at room temperature): δ 0.81(s, C(CH_3)$_3$,18H), 0.96(m, -CH$_2$CH$_2$$CH_2$$CH_2CH_3$, 12H),1.33(s, C($CH_3$)$_3$,9H), 1.42(t,-CH$_2CH_2CH_2CH_2$$CH_3$, 6H), 1.58(s, C($CH_3$)$_3$,9H),1.77-1.97(m,-CH$_2$$CH_2CH_2CH_2CH_3$, 4H) + (t,-CH$_2CH_2$$CH_3$, 3H), 2.21-2.35(m,-CH$_2$$CH_2CH_2CH_2CH_3$, 2H), 3.12(d, Ar$CH_2$Ar, 2H), 3.20(d, Ar$CH_2$Ar, 2H), 3.29(d, Ar$CH_2$Ar, 2H), 4.35 (d, Ar$CH_2$Ar, 2H), 3.78 (t, O$CH_2$, 4H), 3.91 (t, O$CH_2$, 2H), 6.52(d, Ar-$H$, 2H), 7.01(s, Ar-$H$, 2H), 7.12(d, Ar-$H$, 2H), 7.25 (s, Ar-$H$, 2H).

2.3.3. Synthesis of {*p-t*-Bu-calix[4]- (*O*-Pen)$_3$}CoCl (5)

As for 4 but using CoCl$_2$ (0.10 g, 0.61 mmol) pink powder formed(0.28, 48 %), m.p(230 ℃). IR: 3163 m, 2958 s, 2929 w, 2866 m, 1724 m, 1606 w, 1483 s, 1462 w, 1394 m,1363 m, 1292 m, 1249 w, 1201 s, 1116 w, 1035 m, 873 m, 800 m, 526 w, 464 m, 437 w. ^{1}HNMR (CDCl$_3$ at room temperature): δ 0.82(s, C(CH_3)$_3$,18H), 0.98(m, -CH$_2$CH$_2$$CH_2$$CH_2CH_3$, 12H), 1.31(s, C($CH_3$)$_3$,9H), 1.40 (t,- CH$_2CH_2CH_2CH_2$$CH_3$, 6H), 1.57(s, C($CH_3$)$_3$,9H), 1.80-1.98 (m,-CH$_2$$CH_2CH_2CH_2CH_3$, 4H)+ (t,-CH$_2CH_2$$CH_3$, 3H), 2.16-2.32 (m,-CH$_2$$CH_2CH_2CH_2CH_3$, 2H), 3.11(d, Ar$CH_2$Ar, 2H), 3.14(d, Ar$CH_2$Ar, 2H), 3.22(d, Ar$CH_2$Ar, 2H), 4.32 (d, Ar$CH_2$Ar, 2H), 3.73(t, O$CH_2$, 4H), 3.85 (t, O$CH_2$, 2H), 6.50(d, Ar-$H$, 2H), 6.98(s, Ar-$H$, 2H), 7.12(d, Ar-$H$, 2H), 7.24 (s, Ar-$H$, 2H).

2.3.4. Synthesis of {*p-t*-Bu-calix[4]- (*O*-Pen)$_3$}NbCl$_4$ (6)

As for 4 but using NbCl$_5$ (0.16 g, 0.61 mmol) red powder formed(0.50g, 78 %) m.p(250 ℃). IR: 3086w, 3049 m, 3020 w, 2960 s, 2933 m, 2862 w, 1724 s, 1650 w, 1606 m, 1485 s, 1456 w, 1380 m, 1288 s, 1267 m, 1203 s, 1201 s, 1090 m, 1072 m, 877 m, 806 m, 727w, 659 w, 450 m, 420 w. ^{1}HNMR (CDCl$_3$ at room temperature): δ 0.82(s, C(CH_3)$_3$,18H), 0.96(m, -CH$_2$CH$_2$$CH_2$$CH_2CH_3$, 12H) 1.32(s, C($CH_3$)$_3$,9H), 1.43 (t,- CH$_2CH_2CH_2CH_2$$CH_3$, 6H), 1.56(s, C($CH_3$)$_3$,9H),1.81-2.01 (m,-CH$_2$$CH_2CH_2CH_2CH_3$, 4H)+ (t,-CH$_2CH_2$$CH_3$, 3H) 2.22-2.36 (m,-CH$_2$$CH_2CH_2CH_2CH_3$, 2H), 3.14(d, Ar$CH_2$Ar, 2H), 3.19(d, Ar$CH_2$Ar, 2H), 3.21(d, Ar$CH_2$Ar, 2H), 4.35 (d, Ar$CH_2$Ar, 2H), 3.73(t, O$CH_2$, 4H),3.85 (t, O$CH_2$, 2H), 5.66 (s, Ar-$OH$,1 H), 6.51(d, Ar-$H$, 2H), 7.07(s, Ar-$H$, 2H), 7.12 (d, Ar-$H$, 2H), 7.25 (s, Ar-$H$, 2H).

2.4. Polymerization procedure[17]

Polymerization procedures was carried out as. In 5 mL of toluene in a Schlenk tube at 110 ℃ under inert gas a mixture of □-caprolactone (42 mmol), catalysts (0.21 mmol) and benzyl alcohol (0.21 mmol) were added. At the required temperature the Schlenk tube was then placed into an oil bath, then was stirred for one hour. Then the solution was quenched by adding of (0.2 mL) of glacial acetic acid follow by pouring the solution into (200 mL) of methanol. White polymer was formed then collected on filter paper and was dried.

2. Results and discussion

The compound **L^{2}H$_1$** was prepared according to the modified reported approach[16]. It was prepared in good yield percent (62%) by treatment of *p-tert*-butylcalix [4]arene with a (30 times equivalent) of n-pentyliodide in THF. In term of stoichiometry the ligand **L^{2}H$_1$** was prepared by the loss of one (HI) molecules through the reaction. The ^{1}HNMR signals are coherent with the structure for **L^{2}H$_1$**(Figure 1 sup.), singlet at 5.73 ppm revealed hydroxyl group proton. Also, signals at 0.82, 1.32 and 1.55 belong to *tert*-butyl. In addition to signals at 0.96 and 1.39

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assigned by methyl group in the pentyl- moiety (Fig. 1 and 2 supplementary).

2.1. Tripropoxy and their complexes

The new chromium (III) tripropoxy-p-*tert*-butylcalix[4]arene complex{p-t-butyl-calix[4]-(O-Pr)$_3$}Cr(NO$_3$)$_2$ (**1**)} can be isolated as green precipitate(Scheme 1) by the reaction of Cr(NO$_3$)$_3$(**1**) with tripropoxy-p-*tert*-butylcalix[4] in toluene at reflux (1:1 ratio). The infra-red spectrum of (**1**) reviled v(NO$_3$) for the bidentate coordinated nitrate group at 1707 cm^{-1} and 1730 cm^{-1} separated by 25 cm^{-1}[18] and the band at 3500 appeared at the apparent tri-propoxy- p-t-Bu -calix[4]are [16] was disappeared in the complex(Fig. 3 sup.). Complex (**1**) was also identified by ^{1}HNMR, peak at 5.51 ppm in the L^{1}H$_1$was gone in the complex(**1**), chemical shifts of the peaks of the methylene group close to the oxygen atom (*O*-CH$_2$) in the L^{1}H$_1$ are shifted downfield from(2.08-2.23 and 2.26-2.36) ppm to (1.83-1.91 and 1.97-2.05) ppm which attributed to coordinate the oxygen atoms close to the methylene group with the metal(Fig.4sup.).
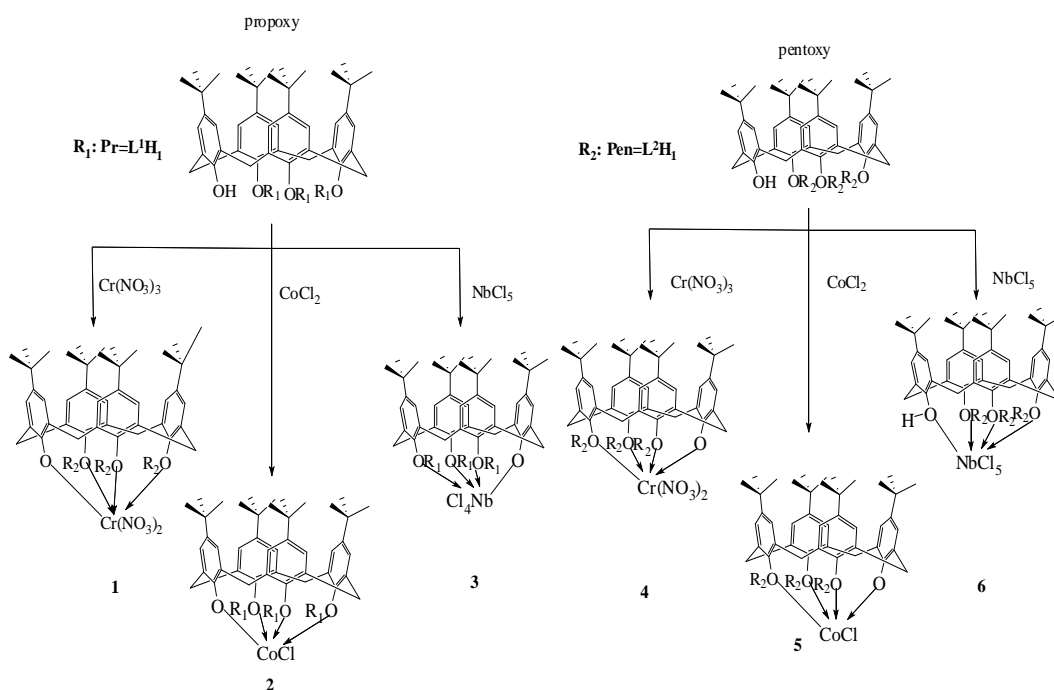
Scheme 1: Ligands and complexes used in this study

The mono-nuclear cobalt tripropoxy-*p*-tert-butylcalix[4]arene and niobium tripropoxy-*p*-tert-butylcalix[4]arene were synthesised *via* the reaction of the tripropoxy-*p*-tert-butylcalix[4]arene ligand, L^{1}H$_1$ in a 1:1 ratio with CoCl$_2$ and NbCl$_5$ respectively at reflux toluene (Scheme 1). Each solution was heated at reflux for 3 hour, after work up the resulting solid was identified by IR and ^{1}HNMR(see experimental section and Fig. 5-8 sup.). By analysing of ^{1}HNMR we have observed that the hydroxyl groups signal in the apparent ligands (L^{1}H$_1$ and L^{2}H$_1$) at around 5 ppm was disappear while the singlet belong to R-OAr (about 3.7 to 3.9) in both ligands were little shifted.

2.2. Tripentoxy and their complexes

Treatment of tripentoxy-*p*-*tert*-butylcalix[4]arene with Cr(NO$_3$)$_3$ in toluene with reflux yields a complex (**4**) in which the chromium attached with two NO$_3$ group and both bidentate mode according to the IR spectrum which revealed bands at 1703 cm^{-1} and 1726 cm^{-1} separated by 23 cm^{-1}[18] , and there is a coordinate bond with adjacent oxygens of (OCH$_2$) moieties because there is shift in NMR peaks in this area (figure 9 and 10 sup.). L^{2}H$_1$ in a 1:1 ratio with CoCl$_2$ and NbCl$_5$ respectively in

refluxed toluene (Scheme 1), after work up the resulting solid was identified by IR and ^{1}HNMR(see experimental section). ^{1}HNMR spectra of **4** and **6** in chloroform-d indicated disappear of hydroxyl group signals in the aromatic ring in the tripentoxy *p-tert*-calix[4]arene, also other signals were shifted due to coordination between ligand with metals. The evidence enough to say there is a coordinate bond between Co and Nb because there a little shift in signal in the ^{1}HNMR (Fig. 11-14 sup.)

3. The use of prepared complexes as catalysis of ring opening polymerisation (ROP) of ε-caprolactone

The Cr, Co and Nb complexes **L[1]H[1]**(1-3) and Cr, Co and Nb complexes (**4-6**) have been tested for their capability to ROP of ε-caprolactone (Table 1). Ring opening polymerization of *ε*-CL*:* experiments were run in the presence of benzyl alcohol (BnOH). On increasing the average molecular weight from tripropoxy-p-tert-butylcalix[4]arene complexes to tripentoxy-p-tert-butylcalix[4]arene complexes this may attributed to the increasing in size of alkyl group lead to intense the positive charge on metals atoms in the complexes, these lead to intense the negative charge on alkyl groups which responsible of the nucleophilic attack on the monomer[19]. Comparing cobalt complex **1** and **4** have higher molecular weight (M_n) as compared with chromium and niobium complexes (**2**, **3**, **5** and **6**) complexes in both systems due to cobalt has highest electronegativity (1.8 Co, 1.6 Cr and 1.6 Nb), the increasing in the negativity of metals of the catalysts containing cobalt is beneficial in terms of

molecular weight (Mn) (runs 2–5 versus 1, 3, 4 and 6), whilst all catalysts perform better in term of yield percent. All polymers (PCLs) obtained have a narrow PDI characteristics (1.13 – 1.26). Fig. 15 in sup. an example of gpc runs.

Table 1. ROP of ε-CL using complexes 1-6

Run[a]	Cat.	Conv.%	Mn^b	PDI[c]
1	**1**	15.8	3780	1.17
2	**2**	8	4370	1.25
3	**3**	98.0	3040	1,13
4	**4**	98.5	4920	1.33
5	**5**	59.0	5450	1.26
6	**6**	92.5	2590	1.41

Conditions: [a]runs were follow under nitrogen in toluene. [b]M_n GPC in THF with a Mark–Houwink factor of 0.56. [c](Mw/Mn) from GPC, t/°c=110 , time 1hour, CL: Cat :BnOH=200:1:1.

4. Conclusion

In conclusion, a series of Chromium(III), Cobalt(II) and Niobium(**V**) tripropoxy/tripentoxy-ptert-butylcalix[4]arene complexes have been synthesised, characterized by IR and ^{1}HNMR spectra, their ability as catalysts for ring opening polymerization of ε-caprolactone by ring opening polymerization was investigated. In term of control all polymer obtained carry on in controlled mode. Some features were suggestive from the results for instance metals have high electronegativity have high activity. Also employ a long chain alkyl group linking with O-alkyl in calix[4]arene was beneficial to increase molecular weight.

5. References

[1] H. Leuchs, Ueber die Glycin-carbonsäure, Berichte der deutschen chemischen Gesellschaft 39(1) (1906) 857-861.

[2] X. Wang, K.-Q. Zhao, Y. Al-Khafaji, S. Mo, T.J. Prior, M.R.J. Elsegood, C. Redshaw, Organoaluminium Complexes Derived from Anilines or Schiff Bases for the Ring-Opening Polymerization of ε-Caprolactone, δ-Valerolactone and rac-Lactide, European Journal of Inorganic Chemistry 2017(13) (2017) 1951-1965.

[3] A.-K. Yahya, P. Timothy J., E. Mark, R. Carl, Molybdenum (Vi) imido complexes derived from chelating phenols: synthesis, characterization and ε-caprolactone rop capability, 2015.

[4] H. Zhou, D. Liu, J. Gega, K. Surowiec, D.W. Purkiss, R.A. Bartsch, Effect of para-substituents on alkaline earth metal ion extraction by proton di-ionizable calix[4]arene-crown-6 ligands in cone, partial-cone and 1,3-alternate conformations, Organic & Biomolecular Chemistry 5(2) (2007) 324-332.

[5] L. Baldini, A. Casnati, F. Sansone, R. Ungaro, Calixarene-based multivalent ligands, Chemical Society Reviews 36(2) (2007) 254-266.

[6] A. Soriente, M. De Rosa, P. La Manna, C. Talotta, C. Gaeta, A. Spinella, P. Neri, Exploiting the p-Bromodienone Route for the Formation and Trapping of Calixarene Oxenium Cations with Enamine Nucleophiles, The Journal of Organic Chemistry 83(11) (2018) 5947-5953.

[7] V.G. Organo, D.M. Rudkevich, Emerging host–guest chemistry of synthetic nanotubes, Chemical Communications (38) (2007) 3891-3899.

[8] Y. Chen, F. Huang, Z.-T. Li, Y. Liu, Controllable macrocyclic supramolecular assemblies in aqueous solution, Science China Chemistry 61(8) (2018) 979-992.

[9] Z. Asfari, J. Harrowfield, P. Thuéry, J. Vicens, Calixarenes as Polyhapto-aromatic Ligands: Alkali Metal Ions and Sulfonated Calixarenes, Supramolecular Chemistry 15(1) (2003) 69-77.

[10] I. Sviben, N. Galić, V. Tomišić, L. Frkanec, Extraction and complexation of alkali and alkaline earth metal cations by lower-rim calix[4]arene diethylene glycol amide derivatives, New Journal of Chemistry 39(8) (2015) 6099-6107.

[11] B. Mokhtari, K. Pourabdollah, Binding and extraction of alkali and alkaline earth metals by nano-baskets of calix[4]arene-1,2-crown-3, Journal of Inclusion Phenomena and Macrocyclic Chemistry 73(1) (2012) 269-277.

[12] W. Śliwa, Calixarene Complexes with Transition Metal Ions, Journal of inclusion phenomena and macrocyclic chemistry 52(1) (2005) 13-37.

[13] P. Murphy, S.J. Dalgarno, M.J. Paterson, Transition Metal Complexes of Calix[4]arene: Theoretical Investigations into Small Guest Binding within the Host Cavity, The Journal of Physical Chemistry A 120(5) (2016) 824-839.

[14] Y. Yang, T.M. Swager, Main-Chain Calix[4]arene Elastomers by Ring-Opening Metathesis Polymerization, Macromolecules 40(21) (2007) 7437-7440.

[15] M.J. Walton, S.J. Lancaster, C. Redshaw, Highly Selective and Immortal Magnesium Calixarene Complexes for the Ring-Opening Polymerization of rac-Lactide, ChemCatChem 6(7) (2014) 1892-1898.

[16] K. Iwamoto, K. Araki, S. Shinkai, Conformations and structures of tetra-O-alkyl-p-tert-butylcalix[4]arenes. How is the conformation of calix[4]arenes immobilized?, The Journal of Organic Chemistry 56(16) (1991) 4955-4962.

[17] Y.F. Al-Khafaji, M.R.J. Elsegood, J.W.A. Frese, C. Redshaw, Ring opening polymerization of lactides and lactones by multimetallic alkyl zinc complexes derived from the acids Ph2C(X)CO2H (X = OH, NH2), RSC Advances 7(8) (2017) 4510-4517.

[18] A.B.P. Lever, E. Mantovani, B.S. Ramaswamy, Infrared Combination Frequencies in Coordination Complexes containing Nitrate Groups in various Coordination Environments. A Probe for the Metal–Nitrate Interaction, Canadian Journal of Chemistry 49(11) (1971) 1957-1964.

[19] O. Nuyken, S.D. Pask, Ring-Opening Polymerization—An Introductory Review, Polymers 5(2) (2013) 361-403.