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Journal of Molecular Catalysis A: Chemical 149 (1999) 125–133

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Calixarenes as a new class of external electron donors in Ziegler–Natta polypropylene catalysts

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Received 9 November 1998; accepted 10 February 1999

Abstract

In this work we have shown that calixarenes form a new type of external donor ligand which can function effectively as a selectivity control agent to increase the yield of isotactic polypropylene in late-generation Ziegler–Natta catalysts. The procatalyst prepared utilized dibutylphthalate as the internal donor to function with the calixarene. We have synthesized and characterized a wide variety of new substituted calixarenes containing hydroxy- and methoxy-end groups. All of these calixarenes were evaluated in the bulk polymerization of propylene and found to increase significantly the amount of i-PP formed relative to reactor runs performed without the calixarene.

Keywords: Calixarene; Ziegler–Natta catalyst; Polypropylene; External donor; Isotacticity

1. Introduction

Despite considerable recent academic and industrial interests in homogeneous, single site catalysts, the fact remains that the vast majority of polyolefins produced commercially are derived from heterogeneous catalysts. In particular, in the case of isotactic polypropylene (i-PP), this stereoregular resin is produced almost exclusively using late-generation, heterogeneous Ziegler–Natta catalysts. While Ziegler–Natta catalysts are broadly defined as mixtures of a metal alkyl of Groups 1–3 and a transition metal salt of Groups 4–10, most Ziegler–Natta catalysts useful in preparing i-PP consist of an ill-defined titanium chloride complex supported on magnesium chloride [1]. This $TiCl_4/MgCl_2$ complex, termed the procatalyst, usually includes an *internal* organic donor ligand in addition to the metal halides. While seemingly simple in preparation, there are literally thousands of minor variations of this preparation reported in the open and patent literatures over the past 40 + years. In earlier generations of Ziegler–Natta catalysts this organic donor is an aromatic monoester such as ethyl benzoate, while more recent Ziegler–Natta catalysts have incorporated aromatic diesters, such as dialkylphthalates, as the internal donor [2]. When tested alone in a polymerization unit, these procatalysts, after activation with the required metal alkyl, do yield polypropylene with an enhanced isotactic fraction relative to the atactic form of polypropy-

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1381-1169/99/$ - see front matter
PII: S1381-1169(99)00147-8

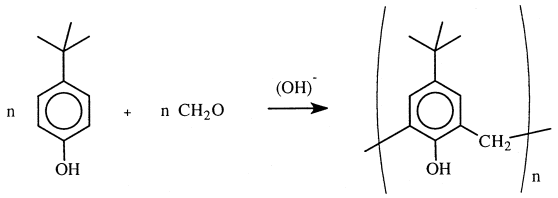


Fig. 1. Generic synthesis of calix[*n*]arenes.

lene. However, the fraction of the polypropylene soluble in boiling *o*-xylene (so-called xylene solubles or XS) of this resin is too high (~30%) to warrant major industrial use. To combat this problem and increase the stereoregularity of the polymer, a supplementary donor molecule is added to the procatalyst and metal alkyl during the course of the polymerization reaction. This *external* donor acts as a *selectivity control agent* and, if properly chosen, can produce i-PP with xylene solubles values as low as 0.5%. There has been significant work reported in the open literature concerning the symbiotic relationship between these internal and external donors. While the exact roles of each component are not yet fully understood, it has been noted that it is the 'pair' of donors which is important and leads to enhanced performance. Internal donors which are monoesters have been shown to work most effectively with external donors that are also monoesters (e.g., ethyl benzoate and ethyl anisate) while diester internal donors function most efficiently with alkoxysilanes as the external donor (e.g., dibutylphthalate and diphenyldimethoxysilane) [3,4]. Much of the work in industry and academia regarding the improvement of Ziegler–Natta catalysts for i-PP has focused on altering the structure of the external donor, and then observing the resulting effects on polymer properties such as yield, XS, molecular weight, and molecular weight distribution. We have been interested in preparing new catalyst systems that vary the external donor. Of particular interest are calixarenes, a family of cyclic oligomers that has a wide range of possible conformations [5]. Our interest in this area arose primarily out of this myriad of potential structures present in these cyclic rings and a curiosity as to whether these compounds could function at all as external electron donors.

Calixarenes are macrocyclic compounds prepared by condensation of phenols and formaldehyde in alkaline conditions in a single step to form cyclic oligomers (Fig. 1). Calixarenes are usually named by a simple convention whereby the number of oligomeric units is denoted by *n* in calix[*n*]arene. Thus, *p-tert*-butylcalix[4]arene indicates the tetrameric para-substituted *t*-butylphenol-derived product. In addition, there are several possible conformations for a particular oligomer, determined by the number of hydroxyl groups pointing in the same direction. For example, Fig. 2 illustrates the four conformations of a calix[4]arene. Substituents present on the phenolic end of a calixarene can dramatically affect conformational preferences. Most of the interest in these compounds in the current literature revolves around the possibilities of preparing host/guest complexes or inclusion

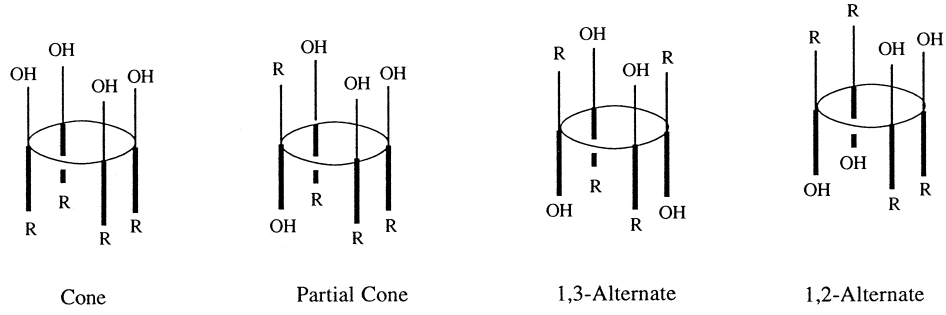


Fig. 2. Conformations for calix[4]arenes.

complexes in the 'basket' formed by the calixarene [6]. The possibility for so many different ring sizes and conformations caused by various substituents allows one to speculate that geometries necessary for reaction as an external donor should be available. Plus, it may be possible to change geometries with minor substituent alterations. Since the residual –OH groups on the phenols can be converted into –OR groups by known chemical routes, donor complexes should be accessible which are more closely related to traditional alkoxysilane donors.

2. Experimental

2.1. Syntheses of calixarenes

The calixarenes evaluated were procured commercially, prepared by methods reported in the literature, or prepared by new syntheses reported here. Abbreviations and structures for the calixarenes are given in Fig. 3. *t*-Butyldimethylcalix[4]arene (*t*BCalixDOM) was purchased from ACROS and used as received. Cyclotetramethylenesilane was obtained from United Chemical Technologies and was used without further purification. Triethylamine was dried and distilled prior to use. The following compounds were prepared according to the literature: *t*-butylcalix[4]arene (*t*BCalix) [7], *t*-butyltetramethylcalix[4]arene (*t*BCalixTOM) [8], *t*-butylpentamethylcalix[5]arene (*t*BCalixPOM) [9], *t*-butyltetramethylcalix[4]arene/LiO_3SCF_3 salt (*t*BCalixTOM · LiO_3SCF_3) [10], *t*-butyl(methylsilyl)methylcalix[4]arene (*t*BCalixSi) [11], *t*-butyl[bis(dimethylsilyl)]calix[4]arene (*t*BuCalixSi2) [10], and *t*-butyl(dimethylsilyl)dihydrocalix[4]arene (*t*BCalixDMS) [10]. (Methylsilyl)methylcalix[4]arene (CalixSi) was prepared analogously to *t*BCalixSi and a more detailed experimental preparation will be given in a future manuscript.

t-Butyl(dimethylsilyl)(methyl)hydrocalix[4]arene (*t*BCalixDMSOM) was prepared as follows. A stirred solution of *t*BCalixDMS (6.50 g, 9.22 mmol) in ether (200 ml) at 0°C was treated with freshly made diazomethane (about 64 mmol) [Technical Information Bulletin Number AL-180 from Aldrich] in ether. The reaction mixture was stirred for 2 h. It was then filtered, and the volatiles were pumped off from the filtrate. The residue was dissolved in hexane, filtered, and the filtrate stored at −30°C overnight yielding the product as a white air-stable solid (4.02 g, 61%). Anal. Calcd. for $C_{47}H_{62}O_4Si$: C, 78.50; H, 8.69. Found: C, 78.38; H, 9.54. ^{1}H NMR ($CDCl_3$): δ −1.76 (s, 3 H, Me), 0.27 (s, 3 H, Me), 1.24 (s, 9 H, *t*-Bu), 1.27 (s, 9 H, *t*-Bu), 1.28 (s, 9 H, *t*-Bu), 1.31 (s, 9 H, *t*-Bu), 3.27 (s, 3 H, OMe), 3.39 (d, $^2J_{HH}$ = 13 Hz, 1 H, CH_2), 3.41 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 3.85 (d, $^2J_{HH}$ = 17 Hz, 1 H, CH_2), 3.95 (d, $^2J_{HH}$ = 13 Hz, 1 H, CH_2), 3.97 (overlapping d, 2 H, CH_2), 4.09 (d, $^2J_{HH}$ = 17 Hz, 1 H, CH_2), 4.20 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 6.68(s, OH, 1 H), 6.89, 6.99, 7.03, 7.11, 7.23 (all d, all $^4J_{HH}$ = 2 Hz, 1 H each, aromatic), 7.07 (overlapping, 3 H, aromatic).

t-Butyl(cyclotetramethylenesilyl)dihydrocalix[4]arene (*t*BuCalixDCPS) was prepared as follows. A stirred suspension of *p-tert*-butylcalix[4]arene (1.298 g, 2.00 mmol) in toluene (65 ml) was treated dropwise with cyclotetramethylenesilane (0.310 g, 2.00 mmol). Then triethylamine (0.405 g, 4.00 mmol) in toluene (5 ml) was added dropwise. The reaction mixture was stirred for 2 days. The resulting mixture was filtered, and the volatiles were pumped off from the filtrate. The residue was dissolved in hot hexane, filtered, and the filtrate stored at −30°C overnight yielding the product as a white air-stable solid (1.20 g, 82%). Anal. Calcd for $C_{48}H_{62}O_4Si$: C, 78.86; H, 8.55. Found: C, 79.25; H, 9.45. ^{1}H NMR ($CDCl_3$): δ −0.32 (t, 2 H, CH_2Si), 0.78 (t, 2 H, CH_2Si), 1.22 (s, 18 H, *t*-Bu), 1.25 (s, 18 H, *t*-Bu), 1.37 (m, 2 H, CH_2 of Si ring), 1.52 (m, 2 H, CH_2 of Si ring), 3.43 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 3.73 (d, $^2J_{HH}$ = 15 Hz, 2 H, CH_2), 3.74 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 3.81 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 4.22 (d, $^2J_{HH}$ = 15 Hz, 2 H, CH_2), 4.29

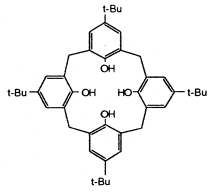
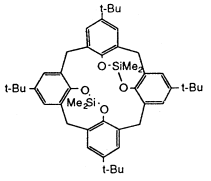
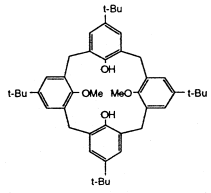
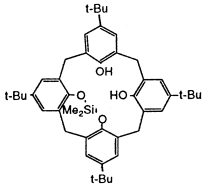
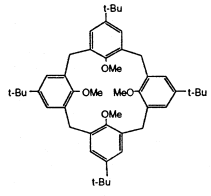
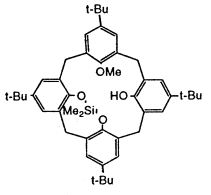
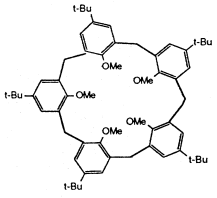
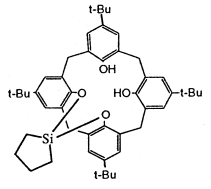
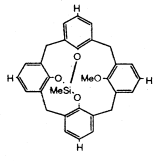
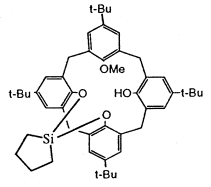
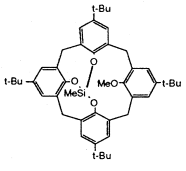
Calixarene	Abbreviation	Calixarene	
	tBCalix		tBCalixSi2
	tBCalixDOM		tBCalixDMS
	tBCalixTOM (with, without LiO_3SCF_3)		tBCalixDMSOM
	tBCalixPOM		tBCalixDCPS
	CalixSi		tBCalixDCPSOM
	tBCalixSi		

Fig. 3. Calixarenes screened as external donors.

(d, $^2J_{HH} = 15$ Hz, 1 H, CH_2), 6.90 (s, 2 H, OH), 6.97, 7.02, 7.07, 7.12 (all d, all $^4J_{HH} = 2$ Hz, 2 H each, aromatic).

t-Butyl(cyclotetramethylenesilyl)(methyl)hydrocalix[4]arene (*t*BCalixDCPSOM) was prepared as follows. A stirred solution of *t*BCal-

ixDCPS (1.00 g, 1.37 mmol) in ether (40 ml) at 0°C was treated with freshly made diazomethane (about 16 mmol) [Technical Information Bulletin Number AL-180 from Aldrich] in ether. The reaction mixture was stirred for 2 h. It was then filtered, and the volatiles were pumped off from the filtrate. The residue was dissolved in hexane, filtered, and the filtrate stored at −30°C overnight yielding the product as a white air-stable solid (0.62, 61%). Anal. Calcd for $C_{49}H_{64}O_4Si$: C, 78.98; H, 8.66. Found: C, 79.03; H, 9.07. ^{1}H NMR ($CDCl_3$): δ −1.87 (m, 1 H, CH_2Si), −1.66 (m, 1 H, CH_2Si), 0.48 (m, 1 H, CH_2Si), 0.52 (m, 1 H, CH_2Si), 0.88 (m, 2 H, CH_2 of Si ring), 0.93 (m, 2 H, CH_2 of Si ring), 1.24 (s, 9 H, *t*-Bu), 1.26 (s, 9 H, *t*-Bu), 1.30 (s, 9 H, *t*-Bu), 1.31 (s, 9 H, *t*-Bu), 3.37 (s, 3 H, OMe), 3.39 (d, $^2J_{HH}$ = 13 Hz, 1 H), 3.43 (d, $^2J_{HH}$ = 13 Hz, 1 H), 3.89 (overlapping d, 2 H), 4.01 (d, $^2J_{HH}$ = 13 Hz, 1 H), 4.07–4.12 (overlapping d, 3 H), 7.03 (s, OH, 1 H), 6.89, 6.99, 7.00, 7.12, 7.28 (all d, all $^4J_{HH}$ = 2 Hz, 1 H each, aromatic), 7.08 (overlapping, 3 H, aromatic). The spectrum indicates some impurities that could not be removed.

2.2. Preparation of procatalyst

The procatalyst used for all evaluations was prepared via a metathesis reaction in chlorobenzene using magnesium ethoxide, diisobutylphthalate, and titanium tetrachloride as described more completely in the 'Preparation of Solid Catalyst Component' section in an earlier patent [12]. After isolation, the procatalyst contained 19.2% magnesium, 2.9% titanium, and 12.1% diisobutylphthalate.

2.3. Analytical

The selectivity to isotactic polymer is determined by measuring the amount of XS polymer present in the polymer as a whole. The test for XS is conducted by dissolving the i-PP polymer in xylene under refluxing conditions. The flask containing the dissolved polymer is then immersed in a water bath at 25°C and maintained without stirring for 1 h, during which time the insoluble portion precipitates. The precipitate is removed by filtration and the solubles content of the filtrate is determined by evaporation of an aliquot followed by drying and weighing of the residue. The XS portion consists mainly of amorphous atactic polypropylene along with low molecular weight crystalline polymer. The diisobutylphthalate content on the final procatalyst was determined by gas chromatography on a sample that had been reacted and solubilized with methoxyethanol. Magnesium and titanium values were determined by atomic absorption spectroscopy. Other elemental analyses were performed by E + R Microanalytical, Parsippany, NJ.

2.4. Autoclave testing

The catalysts were tested according to the following procedure. Liquid propylene (2.7 l) was added to a cooled 4-l autoclave that had been dried under a stream of nitrogen at greater than 90°C. To the stirred autoclave at 62°C were added 17.0 mg of procatalyst (0.01 mmol Ti) as a 5% by weight mineral oil slurry, 1.5 l of hydrogen, 3.6 ml of 5.0% by weight TEAL solution in heptane (1.00 mmol), and the calixarene to be evaluated (0.25 mmol unless otherwise noted) dissolved in toluene. Toluene has been shown in separate experiments to have no deleterious effects on polymerization performance. The polymerization took place for 60 min at 67°C. At the end of the polymerization, the excess propylene was flashed off and the polymer recovered. Drying of the i-PP resin was accomplished by allowing the polymer to sit overnight in a vented hood.

3. Results and discussion

As previously mentioned, late generation Ziegler–Natta catalysts for the manufacture of i-PP utilize alkoxysilanes as the external elec-

tron donor in order to help increase the fraction of stereoregular polymer produced during the polymerization reaction. In commercial units, various alkoxysilanes are used almost exclusively relative to any other external donors, and the increasing number of publications and patents worldwide from a variety of companies that mention various alkoxysilanes testifies to the importance of these donors. Thus, it is of interest to investigate and develop new donor molecules to serve as these external selectivity control agents.

3.1. Preparation of calixarenes

The formulas for these calixarenes are shown in Fig. 3, along with the abbreviations used in the text and Table 1 for the catalyst results. As a point of nomenclature in the text we refer to the parent calixarenes as the hydro-complexes and further substitution reactions are assumed to replace the hydro– on the calixarene, not the hydroxyl. Thus, methylating the parent calixarenes form methylated calixarenes, not methoxycalixarenes, even though the resulting groups are methoxides.

Interestingly, we had difficulty in methylating the remaining hydroxyls on the silylated compounds (*t*BCalixDMS and *t*BCalixDCPS). We were successful only by using diazomethane, and even that method allowed only one of the hydroxyls to be methylated. More traditional routes such as iodomethane with triethylamine or 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) did not give any reaction while reaction with *n*-butyllithium gave decomposition. This difficulty in alkylation of the hydroxyl in the silylated calixarenes is most likely due to unusual conformations in solution adopted by the silylated calixarenes, although this is not known with certainty.

3.2. Reactor testing results

The catalyst results using calixarenes as external donors are shown in Table 1. Additionally, the table also includes the catalyst performance result obtained when *no* external donor is added to the reactor. Given in Table 1 are the abbreviation for the calixarene used (see also Fig. 3), the calixarene/Ti molar ratio ([SCA/Ti]), the triethylaluminum/Ti ratio ([Al/Ti]) which is fixed at 100, the yield of polypropylene in g polymer/g catalyst ([PP/cat]), and the XS data. Without an external donor added the selectivity of the procata-

Table 1
Catalyst performance testing results using calixarenes as external electron donors

Calixarene	[SCA/Ti] (M)	[Al/Ti] (M)	PP/Cat (kg/g cat)	XS (%)
*t*BCalix	25	100	28.2	17.0
*t*BCalixDOM	12.5	100	26.8	17.4
	25	100	14.8	8.4
	50	100	9.4	4.6
*t*BCalixTOM	25	100	26.8	13.6
*t*BCalixTOM (LiO_3SCF_3 salt)	25	100	25.9	13.6
*t*BCalixPOM	25	100	29.6	13.0
CalixSi	25	100	30.9	16.0
*t*BCalixSi	25	100	31.5	14.0
*t*BCalixSi2	25	100	10.8	11.9
*t*BCalixDMS	25	100	27.2	10.9
*t*BCalixDMSOM	25	100	24.0	13.3
*t*BCalixDCPS	25	100	28.1	13.4
*t*BCalixDCPSOM	25	100	28.7	13.4
No external donor (base case)	–	100	29.7	~ 30.0

lyst is poor (the XS of the resulting polymer is ~30%), yet the overall activity remains high at 29.7 kg/g cat. These values establish the baseline case on which to compare the calixarene testing results. It should be noted that while all calixarenes were added to the autoclave as toluene solutions, there is no guarantee that all of the calixarene *stayed* in solution upon addition to the liquid propylene.

The first calixarene examined was *t*BCalix, the parent tetra-hydro calix[4]arene. Immediately apparent in Table 1 is that the addition of *t*BCalix to the procatalyst yields a catalyst that is significantly improved relative to the base case catalyst with no external donor added. In fact, the XS level has dropped from ~30% to 17.0% with no drop in activity. While this drop in XS is not large enough to bring the i-PP formed into the commercially-viable range, the drop is significant enough to validate our initial hypothesis that these calixarenes can indeed serve as selectivity control agents. Our next approach was to replace some or all of the hydro– groups on the calixarene with alkyl groups. The rationale for this was to eliminate the possible reaction of the hydroxyls on the calixarene with the $TiCl_4$ complexed to the procatalyst surface, which upon elimination of HCl forms titanium alkoxides. The reactions with the alkylated calixarenes should form donor–acceptor complexes rather than titanium alkoxides since the HCl elimination pathway is unavailable. It was also of concern that when using the parent hydro-calixarene as an external donor that these –OH groups might react with the $AlEt_3$ cocatalyst, thus eliminating ethane and forming a calixarene-aluminum alkyl species. These resulting species may or may not be able to function as electron donors, although it has been shown that the alkoxysilanes also react with trialkylaluminum to form a donor–acceptor complex [13]. A final reason for alkylation is that the calixarenes are now more similar in structure to the alkoxysilanes used previously. To this end we tested three simple fully alkylated or partially alkylated calixarenes. The fully alkylated calixarenes were the *t*BCalixTOM and *t*BCalixPOM. Also evaluated was the partially alkylated *t*BCalixDOM. Examination of Table 1 shows significantly enhanced selectivity performances for these catalysts relative to the parent tetra-hydro calixarene for the same [SCA/Ti] ratio. For example, the dimethylated calix[4]arene has caused the XS level to drop dramatically from 17.0% to 8.4%. The fully alkylated calixarenes, however, showed a less dramatic drop from the parent calixarene from 17.0% to 13.0–13.6%. While the two fully alkylated calixarenes show no decrease in activity the dimethylated calix[4]arene is markedly less active than the parent hydro-calix[4]arene at the same [SCA/Ti] ratio. This may be due to differences in the amount of hydrogen bonding present in these two calixarenes. *t*BCalix adopts a cone structure in solution with all four hydroxy groups connected with intramolecular hydrogen bonding. *t*BCalixDOM adopts a 1,3-alternate structure in solution, and with the absence of intramolecular hydrogen bonding between the two hydroxy groups it may indicate that these are more available for reaction, presumably with the $TiCl_4$ at the active site, thus having a more pronounced influence on catalyst activity. Another possible reason for the activity change in *t*BCalixDOM relative to *t*BCalixTOM or *t*BCalixPOM may hinge on different structures of the compounds in solution [8]. It may be possible that the conformations of the two methoxy groups in *t*BCalixDOM present in its 1,3-alternate structure, rather than the partial cone structure seen in *t*BCalixTOM, could be of the correct geometry to bind strongly via dative bonds to the procatalyst surface, thus significantly interfering with some of the active sites and acting as a strong poison. To probe this further we performed experiments with both greater and smaller amounts of *t*BCalixDOM as electron donor. These results are also shown in Table 1. Consistent in these experiments is an *increase* in activity using a *lesser* amount of *t*BCalixDOM, indicating the calixarene is acting dramatically as an activity poison. Interest-

ingly, as *t*BCalixDOM is added, concomitant with the activity drop there results a substantial *improvement* in the quality of the i-PP produced —the XS levels drop from 17.4% to 4.6% as the amount of *t*BCalixDOM is increased fourfold. *t*BuCalixTOM and *t*BCalixPOM are significantly more conformationally mobile in solution than *t*BCalixDOM. This behavior may also indicate that donor complexes made by *t*BuCalixTOM and *t*BCalixPOM to the procatalyst surface are not as strong as those made by *t*BCalixDOM.

We next prepared several silyl-substituted calix[4]arenes. The purpose of these experiments was to try to 'cap off' pairs of the hydro– groups on the parent calixarene and form modified electron donors that resembled more traditional alkoxysilane external donors. These silyl-substituted compounds are shown in Fig. 3. In two cases (CalixSi and *t*BCalixSi) we capped off three hydro– groups of the calixarene with a single Me–Si≡ group, leaving one dangling $-OCH_3$ group on the calixarene, presumably in a partial cone conformation. While all of the structures of the other silyl-substituted calixarenes are not known, most likely adopt the 1,2-alternate structure, as has been shown for *t*BCalixSi2 and *t*BCalixDMS [10]. Performance data are shown in Table 1. With the exception of the bis(dimethylsilyl)-capped calixarene (*t*BCalixSi2) the activity data are quite similar to *t*BCalix while the selectivity data offer some improvements into the 10.9–16.0% range from the earlier seen 17.0%. Only in the case of the bis(dimethylsilyl)-capped calixarene is a significant decrease in activity seen.

Lastly, it is interesting to note that we prepared two versions of the tetramethyl calix[4]arene, one with and one without a LiO_3SCF_3 salt coordinated inside the basket cone. The location of the salt is known with certainty due to an X-ray structure [14]. Interestingly, the presence of the LiO_3SCF_3 salt coordinated to the four methoxy groups of the cone-shaped tetramethylcalixarene has no effect on the polymer properties vs. the polymer properties obtained when the calixarene prepared in the absence of the salt was used. This might indicate that the coordination of the calixarene to the catalyst surface is indeed directed away from the upper rim area towards the lower rim, or 'point', of the cone where the methoxy groups are located. However, most likely it may indicate that the lithium triflate salt decomplexes from the calixarene upon addition to the autoclave, leaving identical calixarenes remaining in solution.

4. Conclusions

In this work we have shown that the class of cyclic compounds known as calixarenes form a new type of external donor ligand which can be used as selectivity control agents to increase the yield of i-PP. We have examined a wide range of calixarenes which show a significant variation in the amount of i-PP formed; however, the nature of the i-PP and XS portions formed using each donor remain essentially similar. Furthermore, synthetic modifications to the parent hydro-calixarenes have produced new donors and catalysts with resultant increases in i-PP selectivity into commercially attractive regimes. We would expect that future modifications to the structures of these calixarenes should allow for even higher selectivities to be achieved for i-PP, and work continues to achieve this goal.

Acknowledgements

We wish to thank Mr. G.N. Myhaver for providing expert autoclave assistance in this project. RAK and ML also appreciate funding, especially a UCC research grant to ML, provided by the UCC Polypropylene SHAC® Catalyst Business Center through the PP Catalyst Business Manager, Dr. S.F. Stanley, and by Dr. C.W. Uzelmeier and Dr. D.B. Morse of the PP Research and Development group. Permission to publish from Union Carbide is most gratefully acknowledged.

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