Applications of Calixarenes in Polymer Synthesis

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Summary: The applications of calixarenes in polymer synthesis have been reviewed. Calixarenes have been used as ligands to prepare rare earth calixarene complexes. A series of rare earth calixarene complexes have been synthesized and employed as efficient catalysts for the polymerization of ethylene, styrene, butadiene, propylene oxide, styrene oxide, trimethylene carbonate, and 5,5-dimethyl trimethylene carbonate. On the other hand, the synthesis and characterization of star-shaped polymers with calixarene as core molecules are also described.

Keywords: calixarene; polymer synthesis, rare earth complex, star polymer

Introduction

Calixarenes are cyclic oligomers obtained from the condensation of formaldehyde with *p*-alkylphenols.[1] The number *n* in calix[*n*]arene stands for the *n* phenol units in a calixarene molecule. Calixarenes with four, six or eight *p-tert*-butylphenol units can be easily prepared according to Gutsche's 'one-pot synthesis' method,[2] which are denoted as *p-tert*-butylcalix[*n*] arenes as shown in Scheme 1.

Many calixarene derivatives have been reported with the introduction of functional groups at the phenolic hydroxy group and at the *p*-position with respect to the phenolic hydroxy group, i.e., substituting the original *t*-butyl group. Calixarenes and their derivatives are highly versatile scaffolds for the design of three dimenional (3D) cavities, which can selectively form complexes with guest molecules or ions, and have been regarded as the third generation of host molecule after crown ethers and cyclodextrins in supermolecular chemistry. Many calixarenes and their derivatives can be used as specific ligands for analytical chemistry, sensor techniques, medical diagnostics, and for the synthesis of new materials.

However, in polymer synthesis, calixarenes are rarely studied and reported. There are two main applications of calixarenes in polymer synthesis: i) use of metal calixarene complexes as catalysts for polymerization, and ii) star polymers with a calixarene core. This paper reports a series of rare earth calixarene complexes as catalysts for the polymerization of ethylene, styrene (St), butadiene, propylene oxide, styrene oxide (SO), trimethylene carbonate, and 5,5-dimethyl trimethylene carbonate.

Calixarenes can also be used as multifunctional initiators to prepare star-shaped polymers. The groups of Gnanou and Sawomoto[3–5] have reported the atom transfer radical polymerization (ATRP) of St and methyl methacrylate (MMA) initiated by calixarene halide derivatives as multifunctional initiators to prepare star-shaped polymers. Here we describe the anionic polymerization of optically active *N*-phenylmaleimide derivatives and the ring-opening polymerization of lactones, cyclic carbonates, using calixarenes as multifunctional initiators to prepare star-shaped polymers.

Rare Earth Calixarene Complexes as Polymerization Catalysts[6]

Ethylene Polymerization

Polyethylene is one of the most important synthetic resins. There is an intensive

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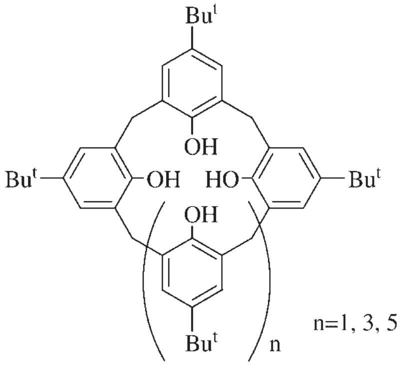


Scheme 1.
The chemical structure of *p-tert*-butylcalix[*n*]arenes.

interest in exploring new and active catalysts for ethylene polymerization. For this purpose, rare eath calixarene complexes have been synthesized. As an example, a neodymium *p-tert*-butylcalix[6]arene complex has been synthesized by the following procedure: 2.469 g (2.54 mmol) of *p-tert*-butylcalix[6]arene and 0.816 g (2.54 mmol) of neodymium isopropoxide were mixed in 50 mL of toluene. The mixture became dark green after stirring for 2 h at room temperature. To ensure the reaction was complet, the mixture was stirred for a further 24 h. The solvent was then distilled off under reduced pressure, and 25 mL of *n*-hexane was introduced to dissolve the product. After filtration, the *n*-hexane was removed under reduced pressure to leave the product. A dark green solid (2.111 g, yield 91%) was obtained after the final drying under vacuum at room temperature. Other rare earth calixarene complexes (C*n*Ln) with various calixarene ligands and rare earth elements have been prepared by a similar method. According to the elemental analysis and NMR spectra, the structures of the rare earth calixarene complexes are shown in Scheme 2.

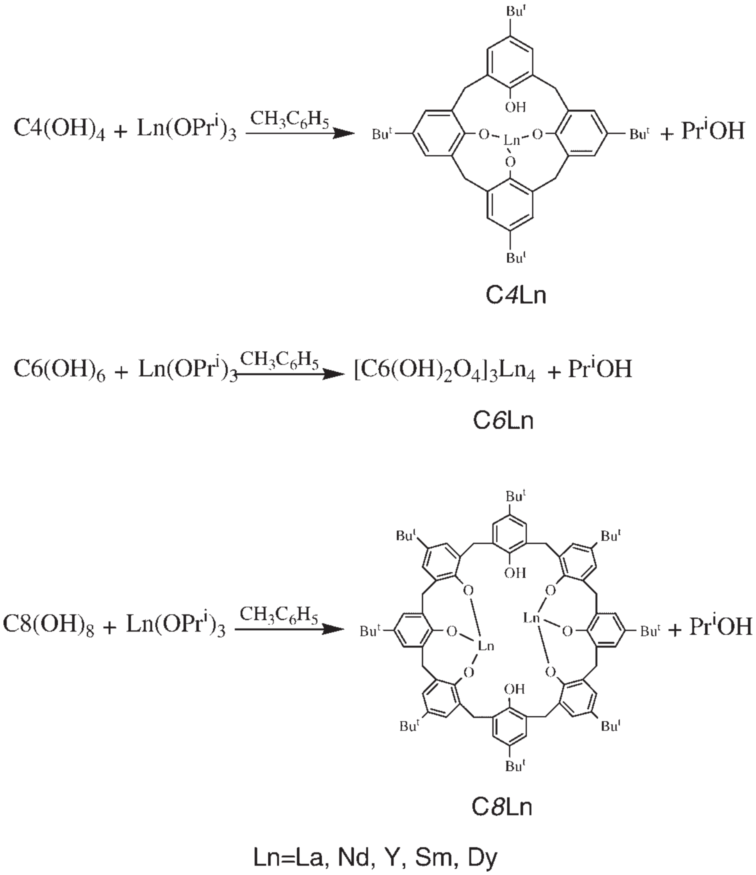
C*n*Ln combined with $Al(iBu)_3$ were found for the first time to be effective homogenous catalysts for ethylene polymerization.[7,8] Eleven rare earth calixarene complexes: C4La, C4Nd, C4Sm, C4Dy, C4Y, C6La, C6Nd, C6Sm, C6Dy, C6Y, C8Nd were used. Table 1 lists the results of ethylene polymerization. It can be concluded that the catalytic activities of the various rare earth calixarene complexes have the following order: C*n*Nd > C*n*Dy > C*n*Sm ≈ C*n*La ≈ C*n*Y, and the catalytic activities of the C*n*Nd with different calixarene ligands decreased as C6Nd > C4Nd > C8Nd. The ^{13}C NMR spectrum of polyethylene prepared by $CnLn/Al(iBu)_3$ only shows one single peak at 28.9 ppm, which indicates the highly linear structure of the polyethylene.

Styrene Polymerization

Ultra-high molecular weight polystyrene can be prepared using C*n*Nd as catalyst with $Mg(nBu)_2$ as cocatalyst in the present of hexamethyl phosphoramide (HMPA).[9,10] The results are shown in Table 2. The catalytic activity sequence is as follows: C6Nd > C4Nd > C8Nd. The polystyrene with a weight-average molecular weight of 2.1×10^6 can be prepared under such conditions: $[Nd] = 8.0 \times 10^{-4}\ mol \cdot L^{-1}$, $[St] = 4.0\ mol \cdot L^{-1}$, $[Mg]/[Nd] = 20$, $[HMPA]/[Nd] = 1$ (molar ratio), 50 °C, 45 min.

Homo- and copolymerization of 4-vinyl pyridine (4-VP) with St were performed using a $C6Nd/Mg(nBu)_2/HMPA$ catalyst system.[11] 4-VP and St copolymers with different 4-VP contents were obtained in good yield. When St was polymerized first for a certain time period, and 4-VP then added, 4-VP and St copolymers with 4.85–23.3 mol-% of 4-VP units were obtained, but when 4-VP and St were added at the same time, the resultant 4-VP and St copolymers had 44.0–66.3 mol-% of 4-VP units.

Another kind of rare earth calixarene complexes, rare earth 5,11,17,23-tetra-*tert*-butyl-25,27-chlorolanthanide dioxyl-26,28-dimethoxyl-calix[4]arene (C4LnCl), were synthesized as shown in Scheme 3. These complexes have also been employed as a catalyst for styrene polymerization with $Mg(nBu)_2$ and HMPA to show a very high catalytic activity (7×10^3 kg PSt/mol Nd · h) and giving polystrene with a very high molecular weight ($>5 \times 10^5$).[12]



Scheme 2.
Syntheses and chemical structures of various rare earth calixarene complexes.

Buta-1,3-diene Polymerization

Neodymium calixarene complexes (C*n*Nd and C*n*NdCl) are efficient homogeneous catalysts for the polymerization of buta-1,3-diene combined with $Al(iBu)_3$, $Al(iBu)_2Cl$, or $Mg(nBu)_2$ as cocatalysts. Polybutadiene with 83–90% *cis*-1,4 content and a molecular weight of $(1–5) \times 10^5$ could be prepared under mild conditions.[13,14]

Table 1.
Effect of various rare earth calixarene complexes on ethylene polymerization.

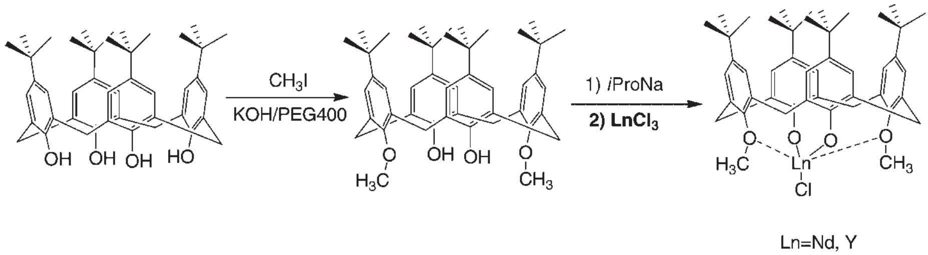
Complexes	PE yield (g)	Catalytic activity (kg PE/mol Nd · h)	$M_v \times 10^{-4}$	m.p. (°C)
C4Y	0.009	0.4	–	–
C4La	0.006	0.3	–	–
C4Sm	0.095	3.8	–	–
C4Dy	0.298	11.9	14.0	128.9
C4Nd	0.715	28.6	14.7	128.3
C6Y	0.131	5,2	157.4	137.5
C6La	0.166	6.6	71.6	131.9
C6Sm	0.095	3.8	95.6	134.7
C6Dy	0.518	20.7	142.7	136.3
C6Nd	0.987	39.5	93.1	136.5
C8Nd	0.211	8.8	97.3	132.8

Polymerization conditions: $[Nd] = 1.0 \times 10^{-3}$ mol/L, [Al]/[Nd] = 15 (molar ratio), 80 °C, 0.5 h, ethylene pressure = 1.2 MPa, toluene 50 mL.

Table 2.
The effect of various CnNd on catalytic activity of styrene bulk polymerization.

CnNd	Polymerization time (min)	Conversion (%)	Activity (kg PSt/mol Nd · h)
C6Nd	65	94	910
C4Nd	65	44	423
C8Nd	190	2	20

Polymerization conditions: St/Nd = 1.0×10^4, [Mg]/[Nd] = 20 (molar ratio), [HMPA]/[Nd] = 1 (molar ratio), 50 °C, 0.5 h.



Scheme 3.
Preparation of C4LnCl.

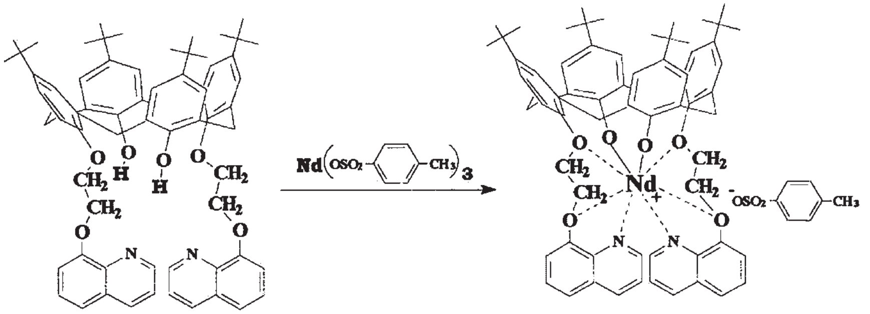
Ring-Opening Polymerization of Epoxy Monomers

It has been found that trinary rare earth coordination catalysts composed of C6Nd, Al(iBu)$_3$, and 2-ethylhexyl phosphonate (P$_{204}$) are effective catalysts for the ring-opening polymerization of SO.[15] The optimum polymerization conditions for preparing poly(styrene oxide) (PSO) with $M_w = 8000$ and 70% conversion with C6Nd/Al(iBu)$_3$/P$_{204}$ were as follows: [Nd] = 9×10^{-3} mol · L^{-1}, [Al]/[Nd] = 70 (molar ratio), 50 °C, 24 h, and hydrogenated benzin as solvent.

A novel neodymium calix[4]arene derivative has been synthesized (Scheme 4) and used as catalyst for propylene oxide polymerization in the presence of Al(iBu)$_3$ and H_2O.[16] Poly(propylene oxide) that is 58–70% isotactic and has a viscosity average molecular weight of 1.7×10^5 can be prepared in good yield (70%) under such conditions: [PO] = 4.0 mol · L^{-1}, [PO]/[Nd] = 300 (molar ratio), [Al]/[Nd] = 12–16 (molar ratio), 70 °C, 22 h, in toluene.

Ring-Opening Polymerization of Cyclic Carbonates

CnLn alone have been developed to catalyze the homopolymerization of trimethylene carbonate (TMC) and 5,5-dimethyltri-



Scheme 4.
Synthesis of a derivative of neodymium calix[4]arene complex.

Table 3.
TMC polymerizations catalyzed by C*n*Ln.

Catalyst	Time (h)	Conv. (%)	M_v (10^4)
C6La	8	75.4	1.56
C6Y	4	42.3	1.13
C6Y	8	74.9	1.23
C4Nd	4	32.6	–
C4Nd	8	88.6	1.65
C6Nd	4	76.6	1.52
C6Nd	8	98.1	2.14
C8Nd	8	88.4	1.22

Conditions: [TMC]/[Ln] = 1000 (molar ratio), 80 °C, bulk.

Table 4.
DTC polymerizations catalyzed by C*n*Ln.

Initiator	Time (h)	Temp. (°C)	Conv. (%)	M_n[a)]	M_n[b)]	MWD[b]
C4Nd	4	80	38.7		–	–
C8Nd	2	80	59.5	5200	4900	1.07
C8Nd	4	80	50.3		–	–
C6Nd	12	60	68.7	5900	4500	1.08
C6Nd	3	80	57.6		–	–
C6Nd	6	80	69.1	5900	5200	1.11
C6Y	4	80	39.0		–	–
C6Y	5	80	42.3		–	–

Polymerization conditions: [DTC]/[Ln] = 200 (molar ratio), [DTC] = 0.64 mol · L^{-1} in toluene;
[a)] Calculated, $M_n = 130 \times \text{Conv} \times ([\text{DTC}]/[\text{Ln}])/3$;
[b)] Measured by GPC.

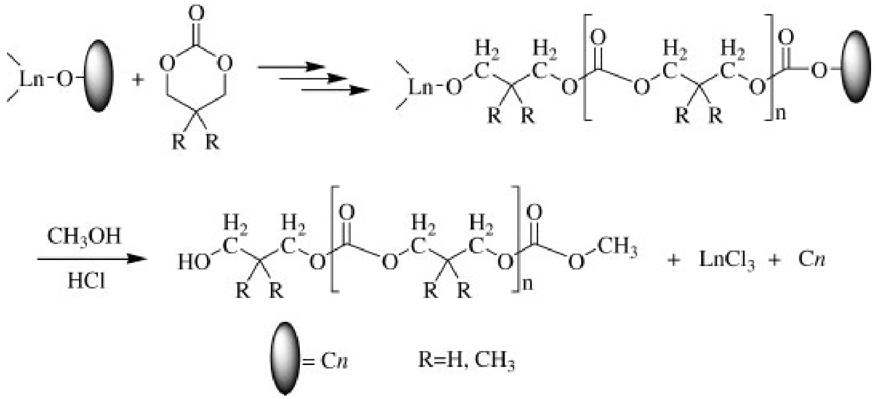
methylene carbonate (DTC), respectively.[17,18] They are efficient single component catalysts for TMC and DTC homopolymerization. Table 3 and Table 4 show the results of the polymerizations.

Based on the polar solvent effect, the end group examination of the polymers, and NMR analyses of the growing chain, it can be concluded that the polymerizations of TMC and DTC initiated by C*n*Ln alone proceeded by a coordination–insertion mechanism as shown in Scheme 5.

The random copolymerization of TMC and DTC were also carried out using C*n*Ln as shown in Table 5.[19] All the five complexes exhibit high catalytic activities and give rise to copolymers with high intrinsic viscosities. Random copolymer with M_w of 14,100 and M_w/M_n of 1.36 was prepared by C6Nd under the following conditions: [TMC+DTC]/[Nd] = 400 (molar ratio), TMC:DTC = 50:50 (molar ratio), 80 °C, 8 h.

The reactivity ratios of TMC and DTC in copolymerizations at 80 °C with C6Nd have been calculated to be $r_{TMC} = 4.68$ and $r_{DTC} = 0.163$ as shown in Figure 1. Diblock copolymers of TMC and DTC could also be obtained with C6Nd by two feeding sequences: either DTC or TMC polymerized first.

A scandium *p-tert*-butylcalix[6]arene complex (C6Sc) has been synthesized from scandium isopropoxide and *p-tert*-butylcalix[6]arene. An EDTA complex-titration of C6Sc revealed that the content of scandium in the calixarene complex was 2.75%, which indicates that every six phenol units of the *p-tert*-butylcalix[6]arene



Scheme 5.
Possible mechanism of TMC and DTC homopolymerization via acyl-oxygen bond cleavage.

Table 5.
TMC and DTC random copolymerization catalyzed by C*n*Ln.

Complex	Conv. (%)	[η] (dL/g)
C4Nd	77.8	0.22
C6Nd	83.2	0.24
C8Nd	75.9	0.15
C6La	83.9	0.16
C6Y	77.1	0.15

Conditions: [TMC+DTC] = 2.0 mol · L^{-1}, [TMC+DTC]/[Ln] = 400 (molar ratio), TMC/DTC = 50: 50 (molar ratio), 80 °C, 8 h, toluene.

have 2.0 OH groups that coordinate to the scandium atom (Scheme 6), which differs from other rare earth *p-tert*-butyl calix[6]arene complexes. This is probably due to the weaker coordination capacity of the scandium atom. The polymerization of DTC using this complex can proceed under mild conditions.[20] PolyDTC with a weight-average molecular weight of 33 700 and a molecular weight distribution of 1.21 can be prepared. Kinetic studies indicate that the polymerization rate is first order with respect to both monomer and initiator concentrations, and the apparent activation energy of the polymerization is 22.7 kJ · mol^{-1}. ^{1}H NMR spectra of the polymer reveal that the monomer ring opens via acyl-oxygen bond cleavage, which leads to an active center of Sc–O.

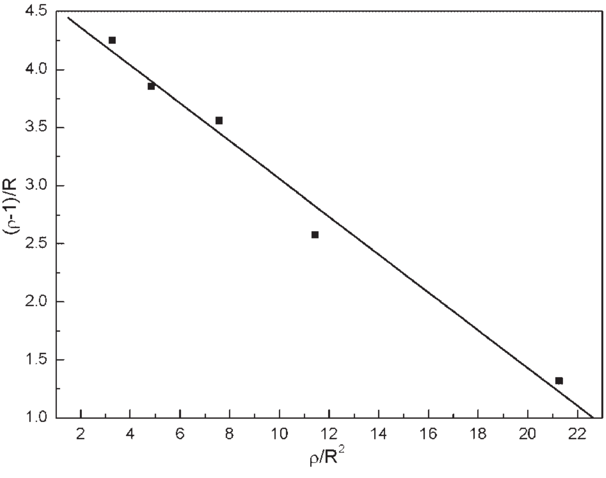
Star Polymers with Calixarene as Core Molecules

Amphiphilic Star-Shaped Polymers using Calix[6]arene as Core Molecule

A star-shaped polymer of six hydrophilic poly(propylene oxide) (PPO) arms was first synthesized by anionic ring-opening polymerization of propylene oxide (PO) onto a calix[6]arene core. An amphiphilic star-shaped six-arm copolymer (PPO-*b*-PDTC) was synthesized via the ring-opening polymerization of DTC initiated by the above star-shaped polymer as macro-initiator and lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) as the catalyst (Scheme 7).[21] The average number of PO and DTC units in each arm could be adjusted by the amount of raw material used.

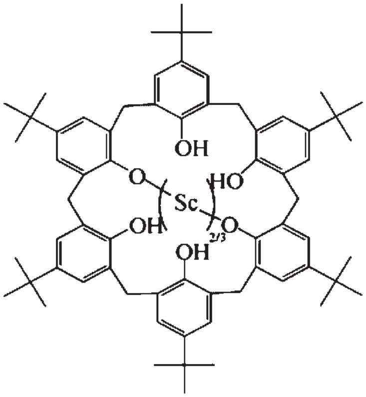
Optically Active Star-Shaped Poly(*N*-phenylmaleimide)s with a Calixarene Core

Two *N*-phenylmaleimide derivatives that bear a chiral oxazoline group, *N*-[*o*-(4-



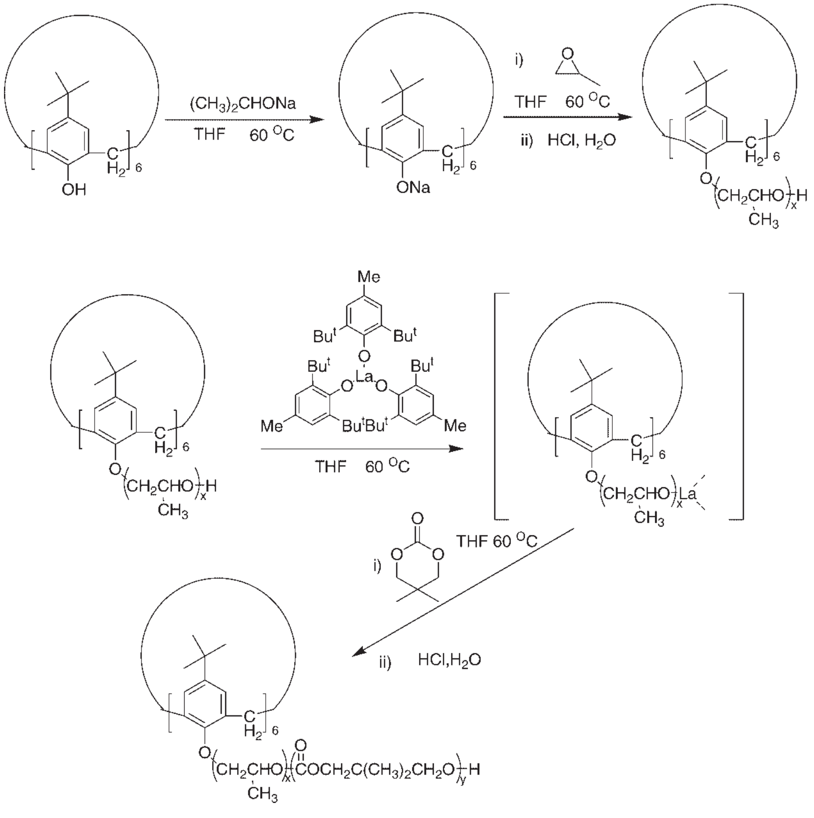
$$\frac{\rho-1}{R}=r_{\mathrm{TMC}}-r_{\mathrm{DTC}}\times\frac{\rho}{R^2}\quad,\quad\rho=\frac{[\mathrm{TMC}]_0}{[\mathrm{DTC}]_0}\quad,\quad R=\frac{[\mathrm{TMC}]_p}{[\mathrm{DTC}]_p}$$

Figure 1.
Reactivity ratio calculation.

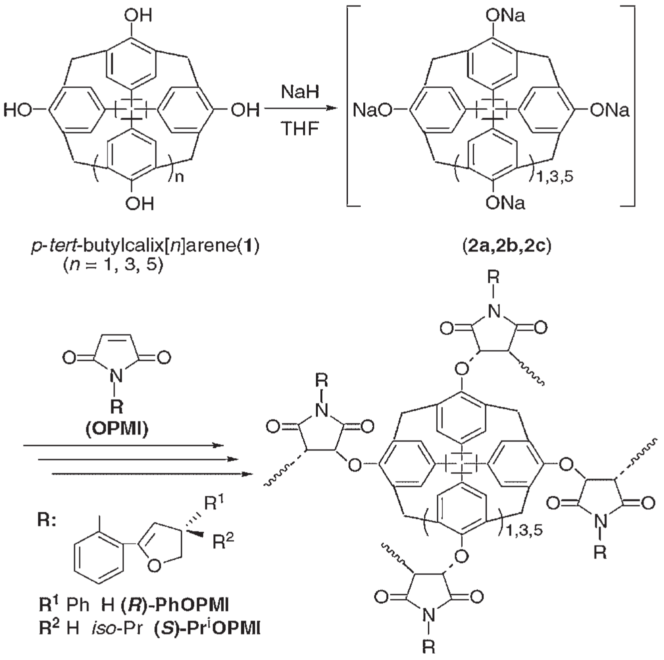


Scheme 6.
Chemical structure of C6Sc.

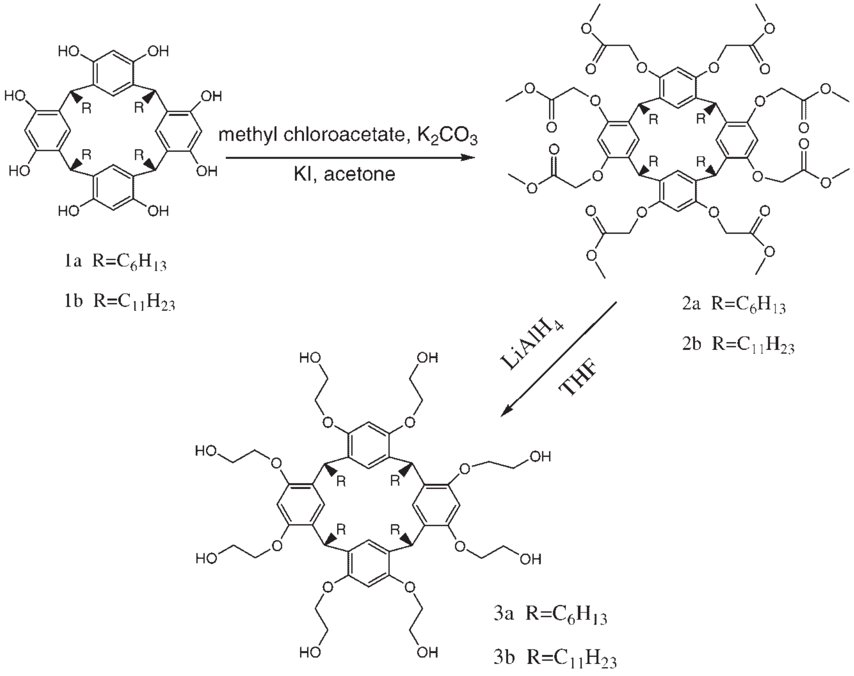
phenyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl] maleimide [(*R*)-PhOPMI] and *N*-[*o*-(4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl]maleimide [(*S*)-PriOPMI], were polymerized using in-situ generated calixarene-based phenolates as initiators via anionic polymerization to yield optically active polymers (Scheme 8).[22] The formation of star-shaped architectures was strongly dependent on both polymerization conditions and calixarene moieties. In the case of polymerization conducted in toluene at 80–100 °C, the arm-chain numbers achieved their respective maxima for the polymers with these multifunctional initiators. In contrast, the polymers obtained by polymerizations at lower temperature possessed fewer arm chains. The structure and chiroptical properties of the macromolecules with calixarene cores were investigated on



Scheme 7.
Synthesis of star-shaped amphiphilic polymers of *p*-*tert*-butylcalix[6]arene core with six PPO-*b*-PDTC arms.



Scheme 8.
Synthesis of optically active star-shaped polymers with calixarene cores via anionic polymerization.

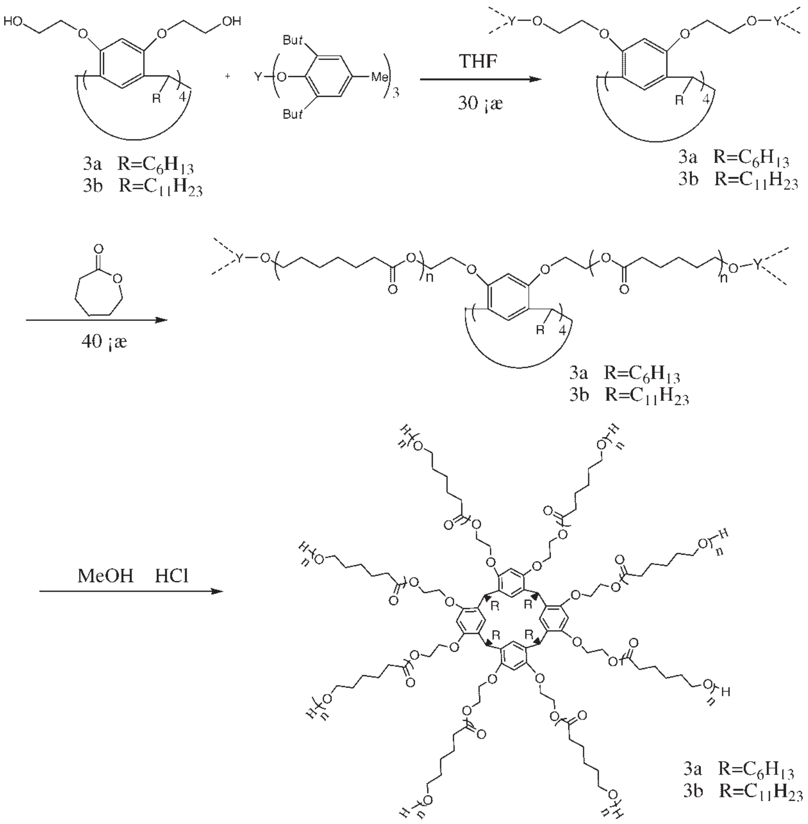


Scheme 9.
Synthetic route for the preparation of two novel resorcinarene-based cores.

the basis of ^{13}C NMR spectroscopy, multi-angular laser light scattering, gel permeation chromatography, and circular dichroism.

Resorcinarene-Centered Eight-Arm Poly(ε-caprolactone) Stars

Resorcinarenes are another group of calixarene synthesized through an acid-catalyzed condensation between resorcinol and an aliphatic or aromatic aldehyde.[23] Generally speaking, resorcinarenes can be considered to contain two parts: one is the phenolic hydroxy groups on the upper rim, and the other one is the R groups from the starting aldehyde on the lower rim. The syntheses of resorcinarene derivatives with various functional groups have been studied in detail, showing that they are useful building blocks in supramolecular chemistry. Tenhu and co-workers introduced the use of functionalized resorcinarenes as ATRP initiators in the polymerizations of *tert*-butyl acrylate and MMA.[24,25] However, to the best of our knowledge, the synthesis of star polymers based on resorcinarene cores via controlled ring-opening polymerization has not been reported. We first synthesized an octafunctional resorcinarene-based precursor (Scheme 9). Well-defined eight-armed star-shaped poly(ε-caprolactone)s (SPCLs) were then prepared via controlled ring-opening polymerization using these precursors as multifunctional initiators in the presence of yttrium tris(2,6-di-tert-butyl-4-methylphe-



Scheme 10.
'Core-First' synthetic strategy for a poly(ε-caprolactone) star by ring-opening polymerization.

Table 6.
Ring-opening polymerization using precursors 3a and 3b (Scheme 10) for SPCLs.

Polymer[a]	[M]/[Precursor] (molar ratio)	[η] (dL/g)	Conv (%)	$M_{n,Cal}$ ($g \cdot mol^{-1}$)[b]	$M_{n,NMR}$ ($g \cdot mol^{-1}$)[c]	$M_{n,SEC}$ ($g \cdot mol^{-1}$)[d]	PDI
SPCL1	55	0.146	90.3	6,800	9,200	18,800	1.28
SPCL2	98	0.162	92.8	11,500	12,600	20,200	1.32
SPCL3	175	0.196	93.9	19,900	20,600	25,300	1.43
SPCL4	200	0.209	95.5	23,000	26,000	32,300	1.46
SPCL5	240	0.210	94.6	27,100	26,300	33,600	1.47
SPCL6	327	0.301	96.0	37,000	36,500	55,000	1.50
SPCL7	55	0.129	91.2	7,200	7,600	17,700	1.26
SPCL8	92	0.135	93.8	11,300	11,500	18,700	1.39
SPCL9	162	0.214	93.1	18,700	19,800	27,000	1.47
SPCL10	207	0.235	94.5	23,800	24,800	35,500	1.49
SPCL11	245	0.236	95.8	28,200	28,500	37,600	1.48
SPCL12	304	0.311	95.2	34,500	36,500	58,000	1.45

Polymerization conditions: THF, $[CL]_0 = 2.0\ mol \cdot L^{-1}$, 40 °C, 4 h;

[a] SPCL1-6 were based on precursor 3a, SPCL7-12 were based on precursor 3b;

[b] Calculated from the feeding molar ratio of [CL]/[Precursor] and conversion;

[c] Calculated from equation: $M_n^{nmr} = \frac{I_d}{I_i} \times \frac{3}{4} \times 114 + M_{precursor}$;

[d] Measured by SEC.

nolate) as catalyst (Scheme 10).[26] A series of SPCLs with well-controlled arm lengths have been successfully synthesized under mild conditions (40 °C) as summarized in Table 6. All the samples were characterized by NMR spectroscopy and size exclusion chromatography.

Conclusions

Rare earth calixarene complexes are efficient catalysts for the polymerization of ethylene, styrene, butadiene, propylene oxide, styrene oxide, trimethylene carbonate, and 5,5-dimethyl trimethylene carbonate. Furthermore, several calixarene derivatives have been employed as multifunctional initiators to prepare star-shaped polymers. More investigations of calixarenes in polymer synthesis are in progress.

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