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Articles

Main-Chain Calix[4]arene Elastomers by Ring-Opening Metathesis Polymerization

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ABSTRACT: Alkene-bridged calix[4]arene monomers were synthesized by ring-closing metathesis (RCM). All the three possible conformers (cone, partial cone, and 1,3-alternate) were used as comonomers with cyclooctene and norbornene in ring-opening metathesis polymerization (ROMP). The resultant polymers were high-molecular-weight, transparent and stretchable materials with high calixarene incorporation (up to 25 mol % or 70 wt %) and low glass transition temperatures.

Calix[4]arenes[1] have been incorporated into main chains of polymeric architectures for various applications, such as sensing,[2] actuation,[3] separation,[4] and nonlinear optics.[5] However, their applications as mechanically active materials utilizing their conformational flexibility remain unexplored. To this end we have been interested in placing calixarenes into a soft and noncrystalline polymer chain, which will allow the stimuli-induced conformational changes. Conventional synthetic methods that have been previously used to make calixarene polymers are based on condensation reactions.[4,5] However, these previous methods did not yield high molecular weight materials with low glass transition temperatures (T_g), which are needed to produce elastomers with good mechanical properties. Some copolymerization approaches additionally suffered from low incorporation efficiencies of calixarene moieties.[4] Another disadvantage is that in most cases protecting groups were necessary due to the multiple reactive sites present in one calixarene molecule. We previously synthesized high-molecular-weight calixarene homopolymers by acetylenic coupling; however this methodology was only efficient for the partial cone (paco) conformer.[6] Here, we report a more versatile and tunable procedure for synthesizing high-molecular-weight and low-T_g calixarene main-chain polymers based upon ring-opening metathesis polymerization (ROMP).

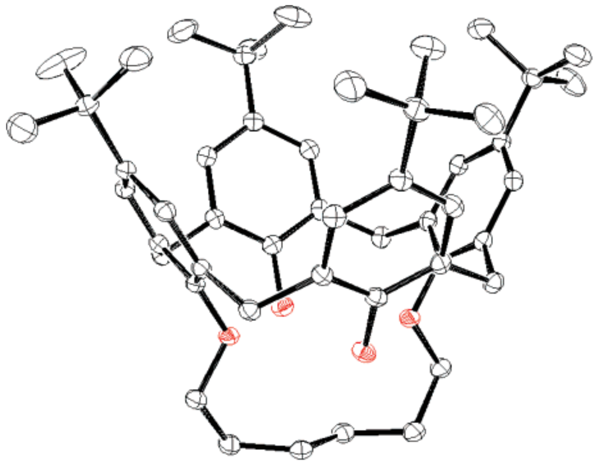
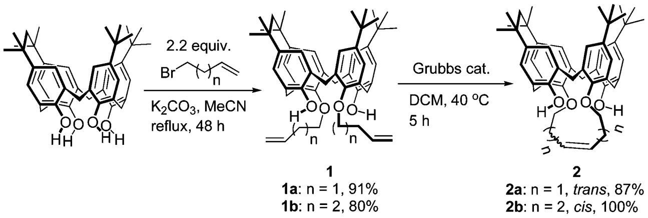


Figure 1. ORTEP drawing of **2a**. Hydrogen atoms are omitted for simplicity.

Scheme 1. Synthesis of Monomers



As shown in Scheme 1, calixarenes **1** with alkyl groups bearing terminal alkenes attached to 1,3-positions of the lower rim were obtained by alkylating *p-tert*-butylcalix[4]arene under weakly basic conditions. A ring-closing metathesis (RCM) reaction with **1b** proceeds in very high (99+%) yield and this result is attributed to the preorganized calixarene scaffold, which positions the two terminal alkene arms in close proximity. With this success we endeavored to use the RCM to create shorter alkene bridge to give calixarene monomer that may have some ring strain for enhanced reactivity in ROMP. We were pleased to find **1a** with shorter all-carbon arms also produced alkene-bridged calixarene **2a** in excellent yield (87%). It is worth noting that the allyl analogue of calixarene **1** ($n = 0$) is not cyclizable. The configuration of the newly formed internal double bond is determined by the length of the bridge and single isomers (either *trans* or *cis*) are observed. The X-ray single-crystal structure of **2a** (Figure 1) reveals that it has a cone conformation with apparent hydrogen bonds between the two free phenols and a *trans* stereochemistry in the alkene bridge. In ^{1}H NMR spectra, the vinyl protons in **2b** have a different coupling constant with the adjacent allylic protons ($J = 5.5$ Hz) as compared to those in **2a** ($J = 3.7$ Hz), therefore we assign the alkene bridge in **2b**

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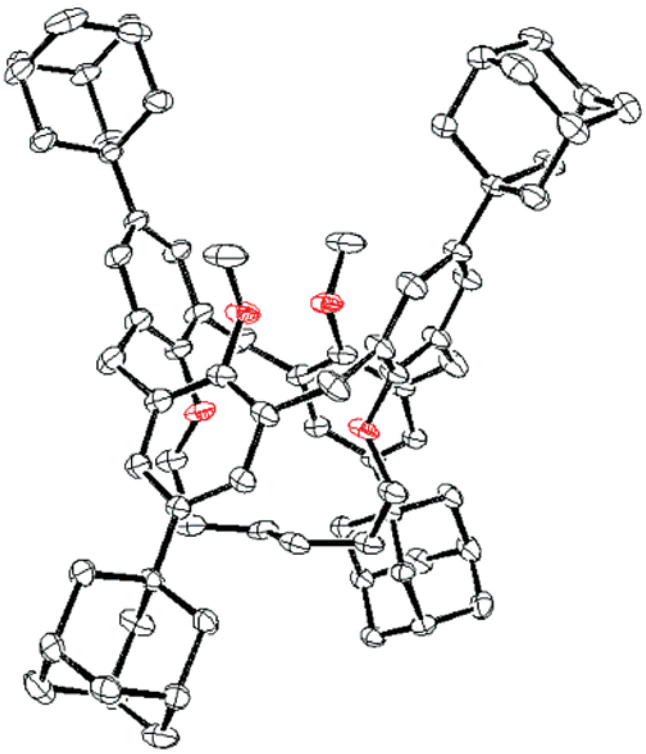
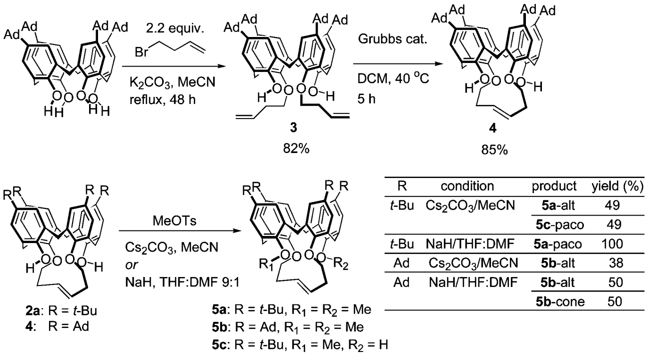


Figure 2. ORTEP drawing of **5b-alt**. Hydrogen atoms are omitted for simplicity.

Scheme 2. Synthesis of Monomers with Ad and Me Substituents



R	condition	product	yield (%)
t-Bu	Cs$_2$CO$_3$/MeCN	**5a**-alt	49
		5c-paco	49
t-Bu	NaH/THF:DMF	**5a**-paco	100
Ad	Cs$_2$CO$_3$/MeCN	**5b**-alt	38
Ad	NaH/THF:DMF	**5b**-alt	50
		5b-cone	50

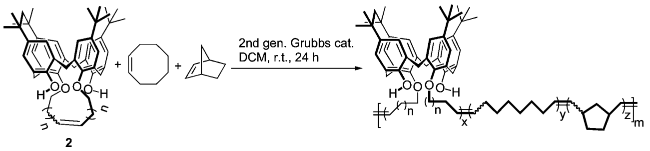
as *cis* configuration.

The two free phenols in **2** did not require protecting groups due to the functional group tolerance of the Grubbs metathesis catalysts.[7] We also investigated calixarene monomers with adamantyl (Ad) groups attached to the upper rim position of the phenyls and the phenols of the lower rim were methylated. As shown in Scheme 2, calixarene **4** with Ad substituents was synthesized in a similar way to **2**. The methylation of the phenols was carried out with Cs$_2$CO$_3$ or NaH base. We expected that removing the hydrogen-bonding would cause the cone conformation of **2a** and **4** to become unstable, and as a result, **5a** and **5b** would be a dynamic mixture of conformers. To our surprise, the conformations were fixed with methylation and the different conformers could be separated by column chromatography. When Cs$_2$CO$_3$ base was used in the methylation of **2a** we obtained a 49% yield of **5a** with a 1,3-alternate (alt) conformation and 49% yield of monomethylated side product **5c** with a paco conformation. When NaH base was used, **5a** was isolated as the paco conformer in quantitative yield. Methylation of **4** using NaH gave **5b** as a 1:1 mixture of alt and cone conformers, and this is contrasted to the low yield of **5b** in the alt conformation obtained when using Cs$_2$CO$_3$. The solution conformations of calix[4]arenes can often be assigned by NMR, however to confirm this and best understand the properties of the conformationally locked **5b-alt**, an X-ray crystal structure was determined (Figure 2).

Main-chain polymers containing calixarenes were synthesized by ROMP with cyclooctene (COE) and/or norbornene (NBE) comonomers, and the results are summarized in Table 1. Calixarene **2b**, which bears a longer bridge, afforded a copolymer with a low molecular weight and low calixarene incorporation (entry 3). The shorter-bridged analogue **2a** displays enhanced ROMP reactivity that may be attributed to small amounts of ring strain. With catalyst/monomer loadings of 1/300, a high-molecular-weight copolymer with high calixarene (**2a**) incorporation was achieved (entry 1). The resulting polymer, **P2a**, shows a subambient T_g, and is an elastomer at room temperature. A T_m was observed due to the semicrystalline nature of the polycyclooctene domain. With lower catalyst loadings, number-average molecular weights over 200 kDa were obtained without sacrificing calixarene incorporation (entry 2). The ring size of the cyclic calixarene alkenes appears to be directly related to the degree of calixarene incorporation into the polymers. The monomer with the smaller ring size (**2a**) displays a higher tendency for incorporated than the monomer with larger ring size (**2b**). NBE was added to eliminate crystallinity and further lower T_g. Indeed, the three-component copolymerization furnished a completely amorphous elastomer with a lower T_g. The calixarene monomers are less reactive than COE and NBE and need to be fed in excess to get the target monomer incorporation in the polymer. However, the unreacted monomer was recovered for reuse in other polymerizations. The polymerization yields calculated that account for recovered calixarene monomer were essentially quantitative.

In contrast to our previous investigations of the acetylenic-coupling-based polymerization, wherein only the paco isomer

Table 1. Synthesis of Polymers



entry	monomer	*n*	M/C[a]	**2**:COE:NBE	M_n (kDa)[b]	M_w (kDa)[b]	PDI[b]	yield (%)[c]	*x*:*y*:*z*[d]	T_g (°C)[e]	T_m (°C)[e]
1	**2a**	1	300	1:4:0	94.5	201.8	2.14	71	1:6.2:0	9	44
2	**2a**	1	1000	1:4:1	209.9	485.8	2.31	64	1:5.1:1.8	−27	n.a.[f]
3	**2b**	2	300	1:3:2	42.9	70.9	1.65	59	1:7.8:5.2	n.d.[g]	n.d.[g]

[a] M/C = [total monomers]/[catalyst]. [b] Molecular weights and polydispersity (PDI) were determined by GPC (polystyrene standards). [c] Yields were calculated based on the total monomers initially fed, although unreacted **2** was recovered. [d] Compositions of the copolymers were determined by ^{1}H NMR (see Supporting Information). [e] Glass transition temperature (T_g) and melting temperature (T_m) were determined by DSC. [f] n.a. = not available. [g] n.d. = not determined.

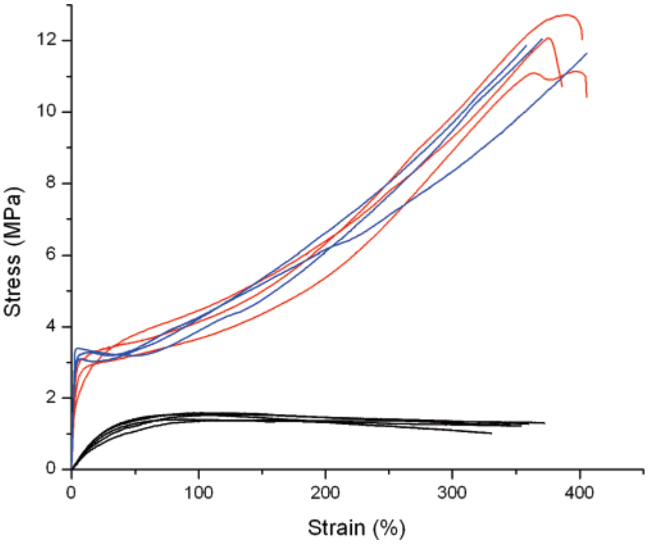
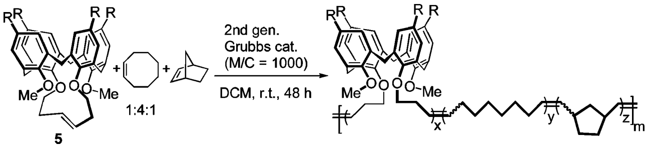


Figure 3. Stress−strain curves of the polymers at 23 °C. Red lines: **P(5a-alt)**, from entry 1, Table 2. Blue lines: **P(5b-cone)**, from entry 4, Table 2. Black lines: **P2a**, from entry 2, Table 1.

Table 2. Scope of ROMP Polymers



entry	monomer	R	M_n (kDa)	M_w (kDa)	PDI	yield (%)	$x{:}(y + z)$	T_g (°C)
1	**5a-alt**	*t*-Bu	188.6	311.8	1.65	91	1:5.6	−6
2	**5a-paco**	*t*-Bu	125.5	221.7	1.77	92	1:4.1	5
3	**5b-alt**	Ad	70.5	97.6	1.38	29	1:5.1	n.d.
4	**5b-cone**	Ad	75.0	116.0	1.55	70	1:4.3	20

polymerized,[6] all of the three possible calix[4]arene conformers (the 1,2-alternate cannot exist geometrically) can be polymerized by ROMP with the COE and NBE comonomers. As shown in Table 2, a range of low glass transition temperatures were achieved and all the copolymers are highly transparent, stretchable, amorphous, and soluble in common organic solvents. The methylated monomers **5** have higher reactivity and give higher calixarene incorporation. The conformational dynamics of calixarenes are sensitive to the substitution of the phenols and alkyl aryl ethers generally slow the interconversion between conformers or lock the calixarene in one conformer. The methylated copolymers show very broad peaks in the room temperature ^{1}H NMR spectra, reflecting the conformational dynamics and diversity of calixarene moieties. The conformation affects the polymerization rates, and monomers in the alt conformation are less reactive, giving lower calixarene incorporation. This reduced reactivity in the alt conformation can be rationalized because the double bond is sandwiched between two aryl rings (a large high-field shift of the vinyl protons can be observed in ^{1}H NMR), making it less accessible to the catalyst. The bulkier Ad group increases steric crowding around the double bond, and therefore **5b-alt** is the least reactive calixarene monomer, giving only 29% yield of the polymer (entry 3).

We also attempted to polymerize calixarenes **1**, which bear terminal alkenes, by acyclic diene metathesis (ADMET)[8] and ring-opening insertion metathesis polymerization (ROIMP).[9] However, oligomers were obtained for both cases. The RCM−ROMP sequence is clearly the best approach to high-molecular-weight polymers. Interestingly, none of the alkene-bridged calixarenes is homopolymerizable and the origins of these results are unclear.

A dynamic mechanical thermal analyzer (DMTA) was used to measure the static stretching properties of materials with relatively small force responses at specific temperatures.[10] Stress−strain curves of the three representative polymers are shown in Figure 3 and the mechanical properties are summarized in Table 3. The calixarenes moieties in **P(5a-alt)** (red lines, Figure 3) and **P(5b-cone)** (blue lines, Figure 3) are conformationally disordered (cone, paco, and 1,3-alternate) due to the absence of hydrogen bonding at the lower rim. In contrast the calixarenes in **P2a** (black lines, Figure 3) have a fixed cone conformation. Although **P(5a-alt)** and **P(5b-cone)** are different in upper rim substitution, molecular weight, calixarene incorporation and T_g, they exhibit very similar tensile behaviors with higher strength and toughness than **P2a**. It is clear that the conformations of the calixarene moieties are key determinates of the mechanical properties. Calixarenes in a fixed cone conformation possess well-defined cavity, however this geometrically restricted feature is not conducive to interactions between neighboring polymer chains. Calixarenes with more dynamic conformations can create more accessible clefts facilitating greater interactions between polymers that may be responsible for the improved strength. The use of “threading” of polymer chains through the molecular clefts on neighboring polymer chains has recently been demonstrated as a mechanism for enhancement of mechanical properties of triptycene-containing polymers.[11] In contrast to the triptycene-containing polymers, which exhibit linear increase of stress along stretching in the later plastic deformation stage,[11] **P(5a-alt)** and **P(5b-cone)** show exponential increase throughout the plastic deformation stage. This phenomenon can be plausibly explained by considering stretch-induced conformational changes of calixarene moieties. Specifically the nature by which the calixarene moieties are incorporated in the main chains should result in coupling of the conformations with strain in the backbone and potentially interconvert thermodynamically more stable paco and cone conformations into the less stable 1,3-alternate structure.[12] Calixarenes in a 1,3-alternate conformation would create the most accessible clefts for molecular threading and thereby create a structure with increased density. In the case of **P2a** stretching may not be able to disrupt hydrogen bonds that fix the cone conformations, so no increase in modulus is exhibited with

Table 3. Mechanical Properties of the Polymers

polymer	Young’s modulus (MPa)	strain at yield (%)	stress at yield (MPa)	strain at break (%)	tensile strength (MPa)	work (J/cm^3)
P(5a-alt)	109.97 ± 18.63	8.85 ± 0.10	2.76 ± 0.34	397.82 ± 10.16	11.98 ± 0.80	26.73 ± 1.62
% increase to **P2a**	2210		126	13	890	486
P(5b-cone)	141.99 ± 14.93	8.29 ± 3.58	3.26 ± 0.15	378.12 ± 24.56	11.85 ± 0.19	24.31 ± 1.75
% increase to **P2a**	2883		167	7	879	433
P2a	4.76 ± 0.61	44.17 ± 6.60	1.22 ± 0.08	352.58 ± 15.80	1.21 ± 0.11	4.56 ± 0.25

plastic deformation, and the stress−strain curve is flat after the initial deformation.

In summary, we have devised an RCM−ROMP route to high-molecular-weight main-chain calixarene elastomers with good mechanical and optical properties. We have also shown that the conformational properties of the calixarene moieties play a crucial role in determining the mechanical properties. We are endeavoring to explore the applications of these novel polymers that utilize their dynamic receptor properties and conformational flexibility.

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Supporting Information Available: Text giving a detailed description of experimental procedures, including figures showing NMR spectra and a table of crystallographic data and crystallographic information files (cif) for **2a** and **5b-alt**. This material is available free of charge via the Internet at http://pubs.acs.org.

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