High dielectric permittivity elastomers: synthesis, processability, and device manufacturing

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ABSTRACT

The development of novel functional dielectric materials can open the doors to major technological innovations with societal impact. Stretchable capacitors transduce electrical into mechanical energy or vice-versa. Over the last 20 years, they have received significant interest from academia and industry. However, this technology still needs both improved dielectrics as well as conductive elastomers to achieve the desired low driving voltage and to realize devices with attractively high sensitivity. The currently most explored dielectric elastomers are polydimethylsiloxanes (PDMS). However, because of their low dielectric permittivity of only 3, the devices made of them require high voltages for operation.

dielectric properties, and selected the most suitable groups to achieve the highest dielectric permittivity, yet sufficiently low glass transition temperature (T_g) to afford an excellent elastomer at room temperature after cross-linking. This research guided us to several promising polar polysiloxane elastomers modified with nitrile and nitroaniline groups, for which the properties were optimized. We reproducibly achieved dielectric elastomers with a dielectric permittivity of about 18. Some respond to a voltage as low as 200 V, while some give very large actuation and have a breakdown field reaching 100 V μm^{-1}. By carefully selecting suitable synthetic chemistry, we could also achieve self-healable high permittivity elastomers. The materials can be processed into thin films by melt pressing. Stack actuators can be easily manufactured manually and give 5.4% actuation at an electric field as low as 3.2 V μm^{-1}. Furthermore, the actuators can self-repair after a breakdown and be recycled after complete failure.

A graphene nanoplatelets (GNPs) composite in PDMS as a conductive electrode was developed via in-situ polymerization. The synthesis and the processing by screen-printing were conducted solvent-free, making this composite the greenest electrode for this technology.

This presentation gives an overview of recent research on improved materials for dielectric elastomer transducers (DETs) conducted at Empa. We are confident that our materials will impact fields including actuators, sensors, energy harvesting, artificial muscles, and soft robotics.

Keywords: high dielectric permittivity elastomers, conductive elastomers, dielectric elastomer actuators

1. INTRODUCTION

Artificial muscles are soft materials that actuate under an external stimulus such as pH, humidity, solvent, light, temperature, magnetic and electric field.[1,2] Dielectric elastomer transducers (DETs) respond to an electric field or to mechanical stress converting electrical into mechanical energy or vice versa.[3] They are superior to other artificial muscles due to their simplicity of operation, fast response time, and tuneable actuation. Additionally, for their operation, a simple battery can, in principle, be used.[4] DETs have a high application potential for soft robots, sensors, and energy harvesters.[5] Two materials decide over their performance, namely elastic dielectrics and conductors. The first should have increased dielectric permittivity, low dielectric and mechanical losses, and be reversibly stretched without hysteresis. The second should be highly elastic with mechanical properties that mimic the elastic dielectric as closely as possible and be sufficiently conductive to prevent resistive heating. Both materials should be printed to give an elastic capacitive device that consists of a thin dielectric layer between two thin conductive films. However, for manufacturing,

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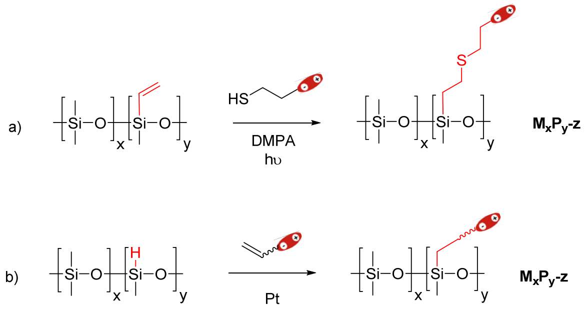
the two materials should be compatible with one another, have desirable processing properties, such as viscosity, and should form defect-free thin films with desirable mechanical, dielectric, and electromechanical properties. Additionally, good compliance and adhesion between the dielectric and the electrode are essential. The functionality and lifetime of the manufactured devices will be affected if one of the parameters/properties are not optimized, and it will be challenging to trace back why a device failed. Often active materials are evaluated in single membrane capacitive devices. While this provides valuable information, it is insufficient to predict the performance of real-life devices, which are composed of many of these membranes stacked on top of each other. We are convinced that it is only these stack actuators which provide the critical information needed for an eventual commercialization. Because commercialization is among our goals, we place considerable attention to the availability and cost of both electrode and the dielectric materials.

Here, we present an overview of the dielectric and conductive elastomers developed by our group, their performance in single membrane capacitors, and the steps undertaken to bring the novel materials into prototype stack devices.

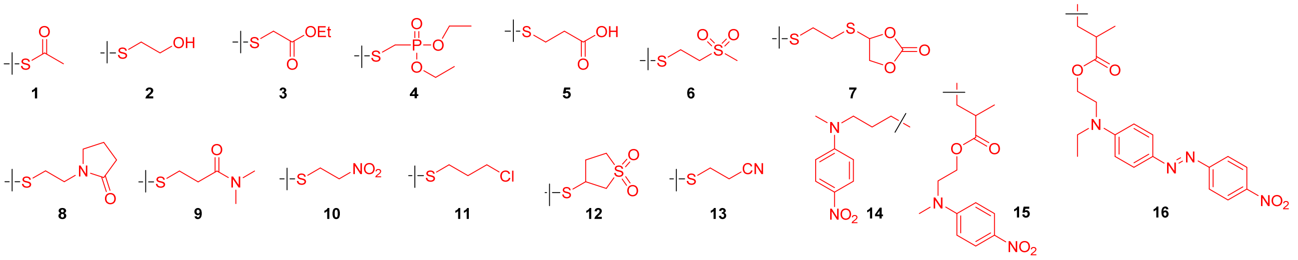
2. SYNTHESIS OF POLYSILOXANES WITH INCREASED DIELECTRIC PERMITTIVITY

Chemical modification with polar groups increases the dielectric permittivity of a polymer, however, the price for it is an increase in the T_g caused by dipole-dipole interaction.[6] Our research is mainly focused on the synthesis of polar silicone elastomers. The siloxane backbone is highly flexible, ensuring low T_g's after modification and it can be easily modified with polar side groups (Scheme 1). Hydrosilylation and thiol-ene reactions of hydrosilyl and vinyl groups, respectively, are often used for such postpolymerization modifications.[7] The first reaction is an addition of the hydrosilyl to the vinyl groups in the presence of Pt catalyst. It requires polar moieties that carry vinyl groups. However, often this reaction cannot be run to completion and the unreacted hydrosilyl groups undergo uncontrolled cross-linking. The thiol-ene reaction requires polar thiols and a UV initiator. The reaction is fast, reliable, and highly efficient. As low molar mass thiols have a pungent smell, it is noted that with increasing the polarity and molar mass, the volatility of thiols decreases and some do not smell at all.



where $\mathbf{M_xP_y}$**-z** for x ≠ 0 and y ≠ 0, and **P-z** for x = 0 and z represents different polar groups used for functionalization

c) Different polar groups z used:



Scheme 1. Synthesis of polar polysiloxanes via a) a thiol-ene reaction or b) a hydrosilylation. Polar moieties are indicated by a red symbol containing '+' and '–' signs. c) different polar groups used for polymer modification.

Using these strategies, we prepared a library of more than 75 polysiloxanes of different polarities (Scheme 1c), which is ideally suited for elucidating structure/property relationships.[8–10] Such exploratory investigations are essential for finding the optimum material for the desired application.

As our focus has always been to have a real application, in the end, the accessibility of the new elastomeric materials received particular attention. Polysiloxanes containing vinyl side groups can be easily synthesized by anionic or cationic polymerization, while those that carry hydrosilyl groups are prepared by cationic polymerization. Anionic polymerization has the advantage that a transient initiator can be used, which is easily deactivated after polymerization by heating at temperatures above 130 °C.[11] Both types of polysiloxanes have routinely been made in our research laboratory on the 100 g-scale.

The thiols that allow introducing polar moieties **1**, **2**, **3**, **5**, **11**, and **13** are commercial, the last is very expensive and therefore, we synthesized it to reduce costs.[8] The other thiols were synthesized using either our synthetic strategies or reported ones.[12] The polysiloxanes modified with thiols **4** and **10**, will be difficult to bring closer to applications because of their demanding synthesis.

The push-pull dipoles **14**-**16** were grafted by a hydrosilylation reaction (Scheme 1b). The respective polar moieties that carry a double bond needed for functionalization were synthesized following reported procedures.[10]

Additionally, the polymers should be stable during purification and drying and should not degrade with time. Unfortunately, although the polysiloxane modified with thiol **7** showed the highest permittivity, this polymer degraded with time, making it less attractive for DETs applications. The polymer modified with thiol **10** underwent cross-linking during drying, likely due to the release of NO_2. The remaining polymers are attractive candidates for further investigations.

The synthesized polymers were investigated by differential scanning calorimetry and broadband impedance spectroscopy. The starting polymer should have a T_g significantly below room temperature to endow a polymer with good elastomeric properties. Figure 1 shows the T_g and the dielectric permittivity of the different polymers synthesized at frequencies above 10 kHz (Table 1), where ion impurities cannot be polarized. Two of the synthesized polymers, **P-12** and **$M_{75}P_{25}$-16,** do not meet this requirement, their T_g was too high. All other polymers have a T_g significantly below room temperature.

A few results are: (a) T_g and dielectric permittivity increase with the amount and the strength of the polar group, yet to a different extent; (b) the dielectric permittivity increases almost linearly with the polar group content and dipole strength of the group, as long as the T_g of the polymer is well below 0 °C. Above this temperature, permittivity decreases. (c) The size of the polar group and the length of the linker between this group and the silicon backbone have an impact on T_g, whereby a low T_g is generally favorable for high permittivity. Larger groups tend to show a stronger increase in T_g than smaller ones and an increased linker length decreases T_g. Larger groups also have an impact on the relaxation frequency, which decreases for bulky groups. The insights gained allowed us to select the most promising polar groups to increase dielectric permittivity.

To conclude, the most promising polar polysiloxanes for DETs applications are accessible, stable, have the lowest T_g, and have the highest dielectric permittivity. A closer look at Figure 1 allowed us to select polysiloxanes modified with **6**, **8**, **9**, **13**, **14**, and **15**. Future work will explore their potential in DETs. As of now, the most explored polar polysiloxanes by our group are those modified with nitrile and nitroaniline groups, the properties of the resulting elastomers will be discussed next.[13–17]

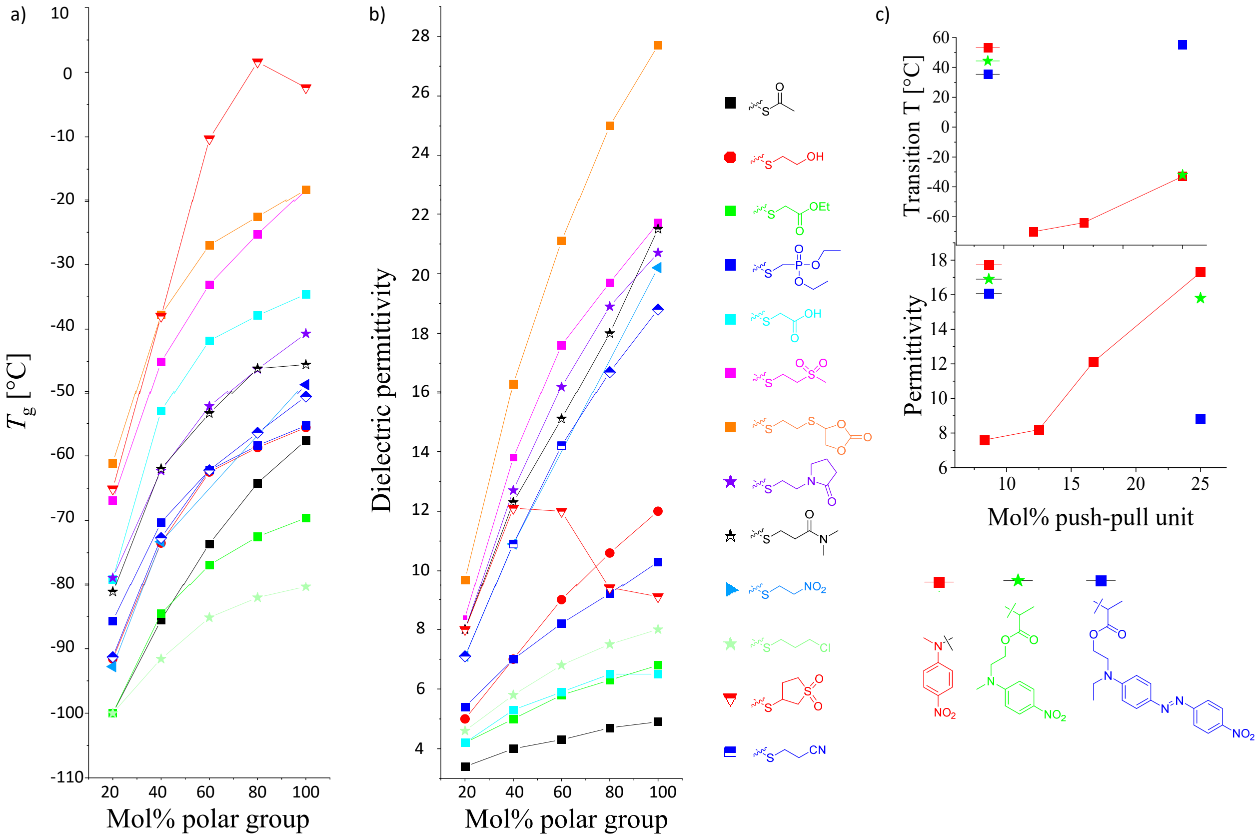
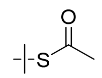
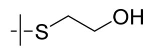
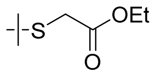
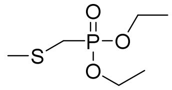
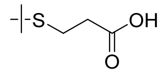
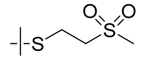
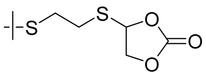
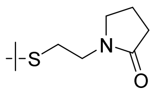
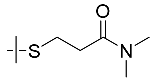
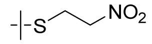
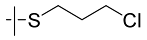
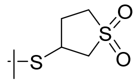
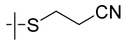
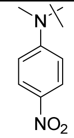
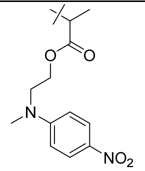
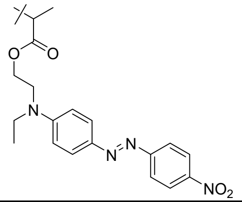


Figure 1. T_g (a) and dielectric permittivity (b) of the polysiloxanes modified with polar thioether groups and the T_g and dielectric permittivity of polysiloxanes modified with polar push-pull groups (c).

Table 1. T_g and room temperature dielectric permittivity at 10 kHz for the different polar polysiloxanes. [ref. 8]

Sample	Polar thiol	T_g [°C]	ε'
M_8P_2-1		< -100	3.4
M_6P_4-1		-85.6	4.0
M_4P_6-1		-73.6	4.3
M_2P_8-1		-64.2	4.7
P-1		-57.6	4.9
M_8P_2-2		-91.6	5.0
M_6P_4-2		-73.5	7.0
M_4P_6-2		-62.5	9.0
M_2P_8-2		-58.7	10.6
P-2		-55.6	12.0
M_8P_2-3		< -100	4.2
M_6P_4-3		-84.6	5.0
M_4P_6-3		-76.9	5.8
M_2P_8-3		-72.5	6.3
P-3		-69.6	6.8
M_8P_2-4		-85.7	5.4
M_6P_4-4		-70.3	7.0
M_4P_6-4		-62.2	8.2
M_2P_8-4		-58.4	9.2
P-4		-55.3	10.3
M_8P_2-5		-79.1	4.2
M_6P_4-5		-53	5.3
M_4p_6-5		-41.8	5.9
M_2p_8-5		-37.9	6.5
P-5		-34.6	6.5
M_8P_2-6		-66.9	8.4
M_6P_4-6		-45.1	13.8
M_4P_6-6		-33.1	17.6
M_2P_8-6		-25.3	19.7
P-6		-18.3	21.7
M_8P_2-7		-61.1	9.7
M_6P_4-7		-37.8	16.3
M_4P_6-7		-27	21.1
M_2P_8-7		-22.6	25.0
P-7		-18.2	27.7
M_8P_2-8		-78.9	8.0
M_6P_4-8		-62.3	12.7
M_4P_6-8		-52.3	16.2
M_2P_8-8		-46.2	18.9
P-8		-40.7	20.7
M_8P_2-9		-81.2	8.0
M_6P_4-9		-62	12.3
M_4P_6-9		-53.4	15.1
M_2P_8-9		-46.1	18.0
P-9		-45.5	21.5
M_8P_2-10		-92.8	7.1
M_6P_4-10		-73.3	10.9
P-10		-48.6	20.2
M_8P_2-11		< -100	4.6
M_6P_4-11		-91.6	5.8
M_4P_6-11		-85.2	6.8
M_2P_8-11		-82.1	7.5
P-11		-80.4	8.0
M_8P_2-12		-65.1	8.0
M_6P_4-12		-38	12.1
M_4P_6-12		-10.3	12.0
M_2P_8-12		1.6	9.4
P-12		-2.4	9.1
M_8P_2-13		-91.3	7.1
M_6P_4-13		-72.7	10.9
M_4P_6-13		-62.2	14.2
M_2P_8-13		-56.4	16.7
P-13		-50.8	18.8
$M_{91.6}P_{8.3}$-14		-	7.6
$M_{87.5}P_{12.5}$-14		-70	8.2
$M_{83.3}P_{16.7}$-14		-64	12.1
$M_{75}P_{25}$-14		-33	17.3
$M_{75}P_{25}$-15		-32	15.8
$M_{75}P_{25}$-16		55.4^a	8.8

[a]This polymer does not show a T_g but rather a T_m is given.

3. SYNTHESIS OF ELASTOMERS WITH INCREASED DIELECTRIC PERMITTIVITY

As a dielectric, any soft elastomer can be used. Decisive over the performance of dielectric elastomer actuators are the mechanical and dielectric properties of the elastomer. While soft elastomers deform easier under electrical and mechanical stress, they also tend to have increased mechanical and dielectric losses and reduced dielectric breakdown field. The pressure generated in an actuator increases linearly with the dielectric permittivity and with the square of the electric field.[3] Thus, to achieve powerful actuators operated at low voltages, one must process the dielectric into very thin films. The dielectric layers in the commercial stack actuator developed by CT Systems have a thickness of 20 µm.[18]

Reducing the thickness of the dielectric below this value is in principle possible, however, it is associated with increased manufacturing costs. Additionally, the thinner the dielectric film gets, the stronger is the influence of the elastic modulus and surface roughness of the electrode. Thus, although reducing the thickness of the dielectric seems straightforward, there are limitations.

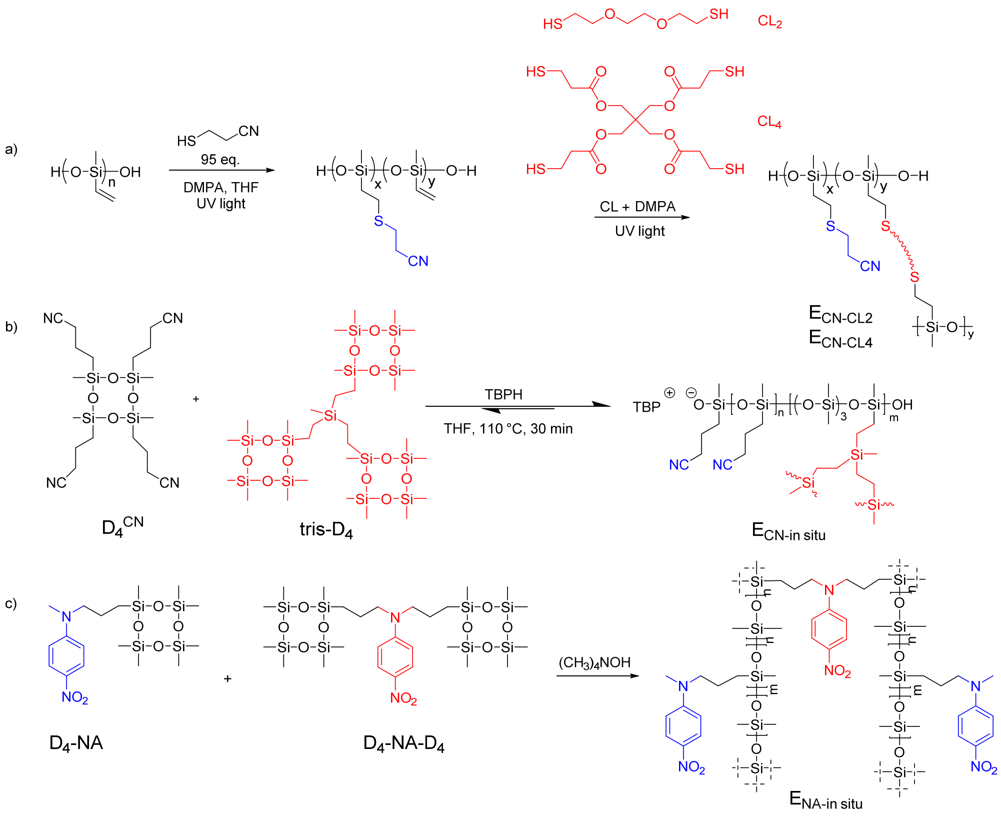
Besides reducing the dielectric film thickness, increasing the electrostatic pressure can be achieved by raising the dielectric permittivity of the elastomers. Elastomers with increased dielectric permittivity can be achieved by blending an elastic matrix with highly polarizable fillers or by cross-linking low T_g polar polymers.[19,20] Early literature suggested that blends with different polarizable fillers significantly enhance permittivity and increase electromechanical sensitivity.[21] For the research conducted by our group to achieve improved high permittivity elastomers using fillers, the reader is referred to literature.[22–27] The approach of cross-linking low T_g polar polymers is superior. It allows achieving soft elastic materials homogenous at the molecular level, with high dielectric permittivity and high dielectric breakdown strength.[16,28,29] The last parameter has a tremendous impact on the power generated by DEAs. It will also impact actuator lifetime since the device can be actuated at electric fields significantly below the critical breakdown field.

In principle, a room temperature polar elastomer can be formed starting from a polymer with a T_g at least 30 °C below the operating temperature. Low T_g high dielectric permittivity polymers are typically highly viscous liquids. To give free-standing films, they have to be cross-linked by an external trigger such as light or temperature. The cross-linking typically increases the T_g and reduces the dielectric permittivity of the formed network, however, this tendency seems to be less pronounced for polysiloxanes than polymers with a C-C backbone.[16,30]

The cross-linking can be done using either side or end groups or in situ polymerization of monomers in the presence of multifunctional monomers.[20] The nature of these groups will decide the conditions needed for cross-linking. Cross-linking should be fast, reliable, quantitative, and should be completed after the trigger is removed.[29] Additionally, air, water, and film thickness should not impact the network formation. Cross-linking of end-groups allows the formation of more defined networks. However, synthesizing polymers with controlled end groups is a great challenge in polymer chemistry and thus has been seldomly used for achieving polar polysiloxane elastomers.[29] The second approach gives less-defined networks with dangling chains and cross-linking points randomly distributed into the network.

Another way of making a network is by in situ polymerization of a monomer in the presence of a multifunctional monomer that functions as a cross-linker. Our group used these strategies to achieve functional dielectric elastomers and the elastomers with the highest dielectric permittivity of about 18 will be discussed here. However, it should be mentioned that elastomers with a permittivity anywhere between 3 and 18 (see Table 1) can be synthesized just by tuning the content of polar groups in the network.[31] It should also be mentioned that an increase in the dielectric permittivity of a material alters the strain at break and increases the ion conductivity. Therefore, one has to find a balance between the different properties by varying the content of polar groups to find a suitable dielectric material for a defined application.

Scheme 2a shows the synthesis of nitrile-modified polysiloxane elastomers as a prototype example. For their synthesis, we used a polymethylvinylsiloxane (M_n = 84 800 g/mol, M_w = 192 000 g/mol, PDI = 2.3) and less than a stoichiometric amount of polar thiol per vinyl groups, thus, purposely leaving some vinyl groups unreacted.[16] They will be needed for subsequent cross-linking into thin films by a thiol-ene reaction. Two different thiols were used as cross-linker: 2,2′-(ethylenedioxy)diethanethiol (CL2) to give material E_{CN-CL2} and pentaerythritol tetrakis (3-mercaptopropionate) (CL4) to give E_{CN-CL4}. After cross-linking, elastomers were obtained that exhibited a low T_g (Table 2). Because the strain at break was rather low, handling thin films and single membrane actuator manufacturing was challenging and we had to learn to manipulate these fragile films. The best protocol is to create the films on a poly(vinyl alcohol) sacrificial layer coated on a glass substrate. Thereafter, the polar silicone film was made on the PVA layer, which was subsequently detached from the glass substrate. This way, we avoided applying any stress to the elastomer and could manipulate films with a thickness even below 20 μm. We then detached the entire ensemble from the glass substrate, fixed the two films between two rigid round frames, and dissolved the sacrificial layer.



Scheme 2. Synthesis of polar siloxane elastomers: a) using vinyl side groups and thiol-ene reaction, b) in situ polymerization of polar cyclosiloxane monomer containing nitrile group (D_4^{CN}) in the presence of a multifunctional monomer (tris-D_4) that functions as a cross-linker, c) in situ polymerization of cyclosiloxane monomer modified with nitroaniline (D_4^{NA}) in the presence of a nitroaniline co-monomer cross-linker (D_4-NA-D_4), that caries two cyclosiloxane groups.

The in situ anionic polymerizations of the polar monomers D_4^{CN} or D_4^{NA} in the presence of a multifunctional cyclosiloxane monomer tris-D_4 or D_4-NA-D_4 (Scheme 2b,c) allowed us to achieve elastomers modified with nitrile ($E_{\text{CN-in situ}}$) and with nitroaniline groups ($E_{\text{NA-in situ}}$). The polar monomers can be easily synthesized using a hydrosilylation reaction either with allyl cyanide (D_4^{CN}) or an allyl functionalized nitroaniline (D_4^{NA} and D_4-NA-D_4). The mechanical properties of the formed network can be easily tuned by the amounts of initiator and cross-linker used. The chain ends in the network are still active, and therefore, these networks behave similarly to thermoplastics. For instance, when heated to elevated temperature, the network softens and flows, while when cooled back to room temperature, the elastic network is reformed. The properties of the most promising materials are included in Table 2.

Table 2. Properties of the most promising polar silicones modified with nitrile and nitroaniline groups: glass transition temperature (T_g), elastic modulus ($Y_{10\%}$), strain at break (s), mechanical loss factor ($\tan\,\delta$), dielectric breakdown field (E_b), and lateral actuation strain at a certain electric field E (s_l @ E).

Elastomer	T_g [°C]	$Y_{10\%}$ [kPa]	s [%]	$\tan\,\delta^{a}$	ε'	E_b [V µm^{-1}]	s_l @E [% @V µm^{-1}]
$E_{\text{CN-CL2}}$	-46	462	82	0.007	18^b	19	13@13
$E_{\text{CN-CL4}}$	-46	862	28	0.002	18^b	74	11.5@26
$E_{\text{CN-in situ}}$	-58.8	202	41	0.007	16.9^b	-	3.5@5.2
$E_{\text{NA-in situ}}$	-37.8	248	122	0.035	18.7^c	9	

[a] At 0.01 Hz; [b] at 10 kHz; [c] at 1 kHz

All materials show a T_g significantly below 0 °C, allowing their use in outdoor applications. They have a rather low elastic modulus, significantly below 1 MPa. The nitrile-modified polysiloxane elastomers have a strain at break below

100%, while the ones modified with nitroaniline have a somewhat better performance. For applications in stack actuators, the mechanical properties of these elastomers are very good, e.g. the mechanical losses are very low, which is important for reliable actuation without hysteresis. Additionally, the strain at break is sufficiently high for actuation. However, for applications where large strains at break are needed, e.g. in stretchable sensors and for energy harvesting, $E_{\text{NA-in situ}}$ has superior properties.

Since all developed materials were relatively soft and had a dielectric permittivity around 18, they responded to rather low electric fields. For instance, actuators constructed from $E_{\text{CN-CL2}}$ gave 13% lateral actuation strain at 13 V μm^{-1} and showed a dielectric breakdown field of 19 V μm^{-1}. Material $E_{\text{CN-CL4}}$ is among the most promising dielectric elastomers. It gives a large lateral actuation of 11.5% at 26 V μm^{-1}. The actuation still occurs above this electric field, but it is out of the plane. This material's average dielectric breakdown field was about 74 V μm^{-1}, but some actuators reached a breakdown field as high as 100 V μm^{-1}. The high dielectric permittivity of 18, makes this elastomer extremely promising for artificial muscle applications at low voltages supposed a way can be found in the future to process this material under solvent-free conditions.

Material $E_{\text{CN-in situ}}$ can be easily prepared on 100 g scale. It reached a lateral strain of 3.8% at a low electric field of 5.2 V μm^{-1}. Material $E_{\text{NA-in situ}}$ has an $Y_{10\%}$ = 248 kPa, a low mechanical loss factor, and gave an actuation strain of 8% at 7.5 V/µm. Because of their low mechanical losses, actuators can be operated for many cycles and show reversible and reliable actuation at rather low voltages (Figure 2). The small hysteresis between cycles is mainly due to the low mechanical loss of all our elastomers. A mechanical loss of 0.1, which is often considered low by materials' scientists, is too high for actuators. Such loss will not allow the material to fully relax back to its initial state after voltage removal and thus will cause hysteresis. Additionally, most actuators self-repair after an electric breakdown.

Despite many published dielectric materials with increased electromechanical sensitivity, the lifetime under cyclic electromechanical tests is rarely reported.[32] It is thus difficult to assess the performance and reliability of those materials in actuators. The lifetime of actuators increases if they can self-repair after a dielectric breakdown. Interestingly, the ability to self-repair was observed for almost all polar silicones developed in our group. During self-repair, part of the dielectric and electrode material is combusted, creating an insulating silica film that eliminates the conductive path through the actuator. Additionally, material $E_{\text{CN-in situ}}$ can also chemically self-heal, and actuators made from it can be recycled even after complete failure, making it extremely attractive for low voltage one-use applications such as in personalized medicine.

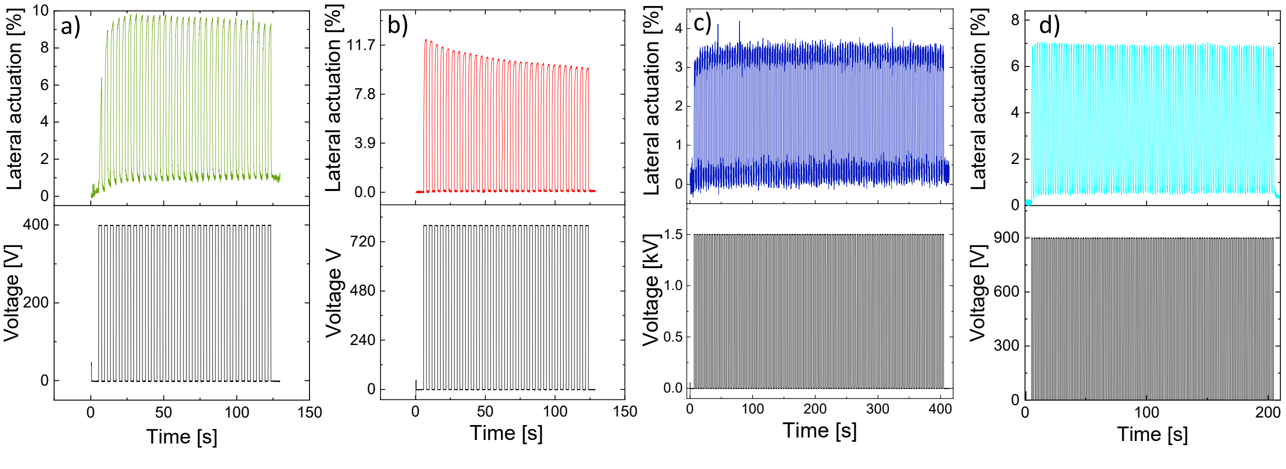


Figure 2. Cyclic electromechanical tests for $E_{\text{CN-CL2}}$ (a), $E_{\text{CN-CL4}}$ (b), $E_{\text{CN-in situ}}$ (c), and $E_{\text{NA-in situ}}$ (d).

4. SYNTHESIS OF CONDUCTIVE ELASTOMERS

For the electromechanical characterization of the new materials developed, we used carbon black powder as an electrode. This electrode material combines good conductivity and easy use with the possibility of applying it on almost any elastomer without affecting the mechanical and dielectric properties.[33]

Single membrane devices generally do not generate sufficient force as required for artificial muscles, even if they are composed of a powerful elastomer and an ideal electrode. Therefore, single membrane actuators are placed on top of each other to form a stack.[34] However, it may well be that the electrode material that was ideal for a single membrane turns out not to be suitable anymore. Typically carbon black electrodes are not compatible with stack manufacturing. A short excursion in the literature shows that the most explored electrode materials in stack actuators are based on carbon nanotubes.[35,36] They are highly conductive, can self-clear a breakdown, and, most importantly, can be easily applied by spraying or printing. However, their major deficiency is toxicity.

This is the point when graphene electrodes come into play as it has reduced toxicity.[37] We used graphene nanoplatelets (GNP) as a filler to increase the conductivity of silicone. There are two different approaches to achieving such conductive composites.

The first strategy uses a PDMS prepolymer blended with 20 wt% GNP.[38] Toluene was used to reduce viscosity and ensure proper mixing of the two components. After adding the cross-linker and the catalyst, the composite was diluted to the desired viscosity for printing. This strategy allowed us to achieve conductive elastomers with a sheet resistance of 0.1 kΩ/□ and a low modulus of elasticity $Y_{10\%}$ = 289 kPa. Because the printing process is rather slow, swelling of the conductive ink was no issue when printed on the dielectric substrate. Actuators made with this electrode showed very good performance and could also self-repair after a dielectric breakdown. The main disadvantage of this composite approach is the necessity of using a solvent and the difficulty in tuning the mechanical properties.

The second strategy uses a dispersion of GNPs in octamethylcyclotetrasiloxane (D_4) (a low viscosity monomer), which is thereafter polymerized by anionic ring-opening polymerization run to equilibrium at 110 °C for 1 h. Thereafter, a multifunctional cyclosiloxane monomer (tris-D_4) that functions as a cross-linker was added at room temperature. The composite was applied on the dielectric by screen-printing three times. The mechanical properties of the composites can be easily tuned just by the addition of a different amount of multifunctional monomer cross-linker. The best material shows conductivity σ= 8.2 S·cm^{-1}, Young's modulus $Y_{10\%}$ = 167 kPa, and strain at break s = 305%. The electrode withstands large uniaxial strains without delamination, shows no conductivity losses during repeated operation (500 000 cycles at RT), and has an excellent recovery of electrical properties upon being stretched at strains of up to 180%. The electrode material allowed us to manufacture reliable capacitive sensors (Figure 3), which can be stretched for thousands of cycles without degradation. The sensors can be reliably operated from low frequencies up to 5 Hz. The developed electrode was also investigated in stack actuators, as will be discussed next.

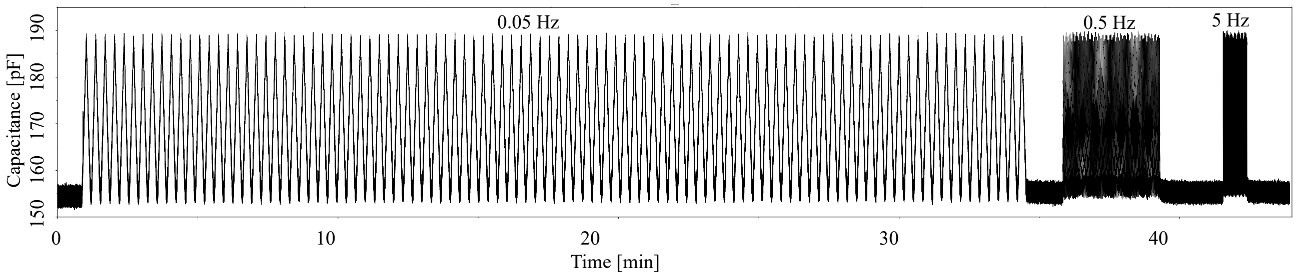


Figure 3. Change in capacitance over 100 cycles at 50% strain and different frequencies of 0.05 Hz, 0.5 Hz, and 5 Hz for a sensor having PDMS as dielectric.

5. STACK ACTUATORS WITH SCREEN-PRINTED ELECTRODES

Placing single membrane actuators on top of each other results in a stack actuator.[39–43] The force generated by the stack increases with the dielectric permittivity, the square of the inverse thickness of the dielectric layer, and also the number of active layers.[44] There are only a limited number of stack actuators reported in the literature, where novel non-commercial materials have been investigated.[36,45] This is mainly due to the great challenges faced when manufacturing robust layered structures from different materials without an adequate processing infrastructure. Therefore, only a limited number of groups undertook research in this direction. The most common way to manufacture stacks is manually, but other ways of manufacturing have been explored. They include blade coating the dielectric and spray coating the electrode, spin-coating the dielectric, and spray coating the electrode through a shadow mask. We recently showed that stack actuators can be efficiently prepared by slot-die coating the dielectric and subsequent spray coating of the electrode. While the dielectric material used was not yet a high dielectric permittivity silicone in the initial phase, the developed process can be easily extended to achieve silicone-based stack actuators.[30]

We used two different silicone-based dielectric materials to construct the stacks: a self-made PDMS elastomer and a nitrile-modified silicone $E_{\text{CN-in situ}}$ with a permittivity of 18.

The first dielectric was made by polymerizing D_4 monomer with the transient initiator tetrabutylphosphonium hydroxide (TBPH) at 110 °C. After the material was cooled to room temperature, the multifunctional monomer that functions as a cross-linker was added. The resulting dielectric mixture was blade coated on a Teflon substrate and cross-linked by heating to elevated temperatures. The dielectric films had a thickness of 165 µm and were cut into pieces with a size of 1.5 cm × 1.5 cm.

The electrode GNP composite prepared by the in-situ process described above was then screen-printed three times on a Teflon substrate to achieve a homogenous electrode. This afforded conductive stripes 1.5 cm wide and 19.5 cm long with a thickness of 55 µm. These stripes were cut in 1.5 cm × 1 cm pieces.

In the next step, both electrode and dielectric were placed on top of one another in an alternating fashion, as illustrated in Figure 4a. The process was repeated until 11 dielectric and 12 electrode layers had been achieved. The active area of the resulting stack actuator was 1 × 1 cm and its thickness amounted to 2590 µm. It was tested at 1 Hz for 90 cycles at voltages up to 4000 V (24 V μm^{-1}) and gave reversible actuation (Figure 4b).

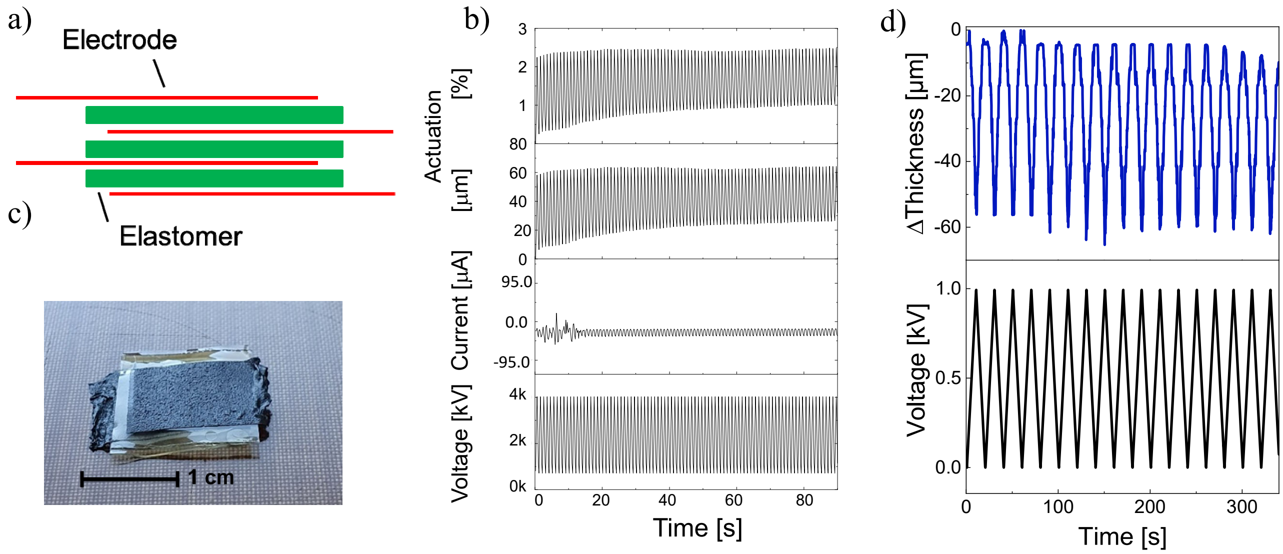


Figure 4. Putting stack actuators to work. The alternating arrangement of electrode and dielectric to form a stack actuator (a). Actuation at 4000 V of a self-made PDMS-based stack actuator tested at 1 Hz for 90 cycles at voltages up to 4000 V (24 V μm^{-1}) (b). Photo of a stack actuator prepared from three active layers of elastomer $E_{\text{CN-in situ}}$ and four electrode layers made from PDMS/GNPs (c). A stack actuator with three active layers of elastomer $E_{\text{CN-in situ}}$ (310 µm each) at an electric field of 3.2 V μm^{-1} shows a thickness change of 56±2 µm corresponding to a relative actuation of 5.4±0.2% (d).

A similar process was used for the manufacturing of stack actuators constructed from $E_{\text{CN-in situ}}$, except that the dielectric films were processed by melt pressing. The stack consisted of three active layers of dielectric elastomer and four layers of the electrode (Figure 4c). We tested the actuator performance at a voltage of 1000 V and a frequency of 25 mHz (Figure 4d). The actuator shows an average thickness change of 56±2 µm corresponding to an actuation of 5.4±0.2% at a very low electric field of 3.2 V μm^{-1}. The small increase of the baseline is attributed to the viscoelastic losses of the dielectric elastomer. This is the first stack actuator with high-permittivity polysiloxanes as dielectric reported to the best of our knowledge.

CONCLUSION

Tremendous research has been invested in DETs development with contributions from engineers, physicists, materials scientists, polymer chemists, and chemists. While many ingenious devices were proposed, most of them are based on commercial products designed to meet the properties for a different application. Additionally, several dielectric elastomers and conductive electrodes are available and their potential should be explored not only in single layer capacitors but also in stack devices. Additionally, the materials should be tested regarding their lifetime in electromechanical tests. Furthermore, materials to be used for stack actuator manufacturing have to be compatible with the processes used and should not interfere with one another.

The strong interdisciplinarity of this research field makes it challenging to bridge novel materials with applications and bring the DETs to the next level, namely improved DETs performance using materials designed for this application. Future progress in this field would be possible only when engineers start working with those developing materials.

Our group used a systematic synthetic strategy to elucidate different polar groups' impact on the dielectric properties of polysiloxanes. Among the most promising polar groups are nitrile and nitroaniline. Both groups allowed the formation of elastomers with a dielectric permittivity that can reach a maximum value of 18. Additionally, the dielectric permittivity of these polysiloxanes can be easily tuned from 3 to 18, just by tuning the amount of polar nitrile and nitroaniline groups incorporated. Furthermore, we achieved elastomers that respond to a low voltage of 200 V and elastomers with a dielectric permittivity of 18 and dielectric breakdown fields that can reach 100 V μm^{-1} giving extremely large actuation. We also achieved elastomers with a permittivity of 18 that can self-heal after mechanical damage, self-repair after a dielectric breakdown, and can be fully recycled after complete failure.

We developed a solvent-free process for a highly elastic electrode with a $\sigma = 8.2$ $S \cdot cm^{-1}$, Young's modulus $Y_{10\%} = 167$ kPa, and strain at break $s = 305\%$. The electrode can be applied by screen printing on any substrate that withstands 130-140 °C. It was used to manufacture stack actuators using PDMS and silicones with a permittivity of 18. The one with the high permittivity silicone as a dielectric was operated at 1000 V and gave a change in stack thickness of 5.4%.

Future work will be invested in increasing the processability of both dielectric and electrode materials such that stack actuators consisting of ultrathin layers are available.

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