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Soft Polydimethylsiloxane Thin Elastomeric Films by In-situ Polymerization to Be Used as Dielectricum in Actuators^a

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A low viscosity, solvent free process for the fabrication of thin silicone films for dielectric elastomer actuators is presented. Octamethylcyclotetrasiloxane and specially designed co-monomers that function as cross-linkers were pre-polymerized to a liquid of low viscosity. This liquid is used to prepare thin films which are then fully polymerized to a highly transparent, cross-linked elastomer. The mechanical and electromechanical properties of the films are easily tuned by altering the amount of cross-linker co-monomer used.

FIGURE FOR ToC_ABSTRACT

^a **Supporting Information** is available online from the Wiley Online Library or from the author.

1. Introduction

Cross-linked polydimethylsiloxanes (PDMSs) also named silicones are important materials that found applications ranging from electronics to personal care products.¹ Their large application potential is mainly due to their excellent properties including high flexibility, good mechanical properties over a wide temperature and frequency range, resistance to oxygen, ozone, and sunlight.²

Most recently silicones caught the attention of the dielectric elastomer actuator (DEA) community where they are used as dielectricum.³ DEA are stretchable capacitors made of a thin elastomeric film coated with two electrodes. When the electrodes are charged, the elastomeric film undergo elongation, converting electrical energy directly into mechanical work (Figure 1).⁴ Due to their simple working principle, DEA could find a large number of applications including actuators, optical devices, infusion pumps, robotics, energy harvesting, sensors, muscle replacement, to name a few.⁵

Figure 1. Cross-section of the non-activated (left) and the activated states of a dielectric elastomer actuator (right).

Silicones as dielectricum for actuators should have good elastic and insulating properties including: high strain at break, high tear strength, low elastic moduli, low viscoelastic losses, low conductivity and high breakdown field. Additionally, they should allow formation of defect free, thin films that do not change their properties in time.⁶ PDMSs are liquids at room temperature. They can be converted into materials with good elastic properties when cross-linked. Low molecular weight (M_w) PDMSs allow formation of highly cross-linked, stiff materials, while high M_w PDMSs provide access to lightly cross-linked soft materials. Soft silicones can be actuated at a lower voltage than stiffer one. Therefore, soft silicones with low

moduli of elasticity are attractive candidates for actuation. Unfortunately, high M_w PDMSs tend to have high viscosity which is detrimental for some processing, e.g. preparation of thin films for DEA applications. To avoid introduction of defects in the film like solid particles and air bubbles, a filtration and degassing step is required. For both steps a low viscosity formulation is of advantage.⁷

To lower the viscosity of high M_w PDMS, solvents are used and the films are formed by letting the solvent evaporate while cross-linking. Such process is noneconomic and environmentally unfriendly. Additionally, some of the solvents are also difficult to remove and therefore might alter the material's properties. Additionally, the films might shrink after solvent evaporation, or when multiple layers are printed, like e.g. in stacked actuators, the solvent can swell and deform the layers.⁸ The viscosity problem was overcome by using low viscosity formulations where the PDMS chain extension and the cross-linking are done in one step. For this typically two components are mixed shortly before use. Once mixed, the cross-linking reaction starts and therefore limited amount of time is left for processing.

Another concern in actuators is aging of the dielectricum which results in unfavorable changes of mechanical properties. Such changes have a direct impact on the actuation strain at a defined electric field and thus on actuator reliability. Since silicones are resistant to oxidation, the alteration of the mechanical properties are most likely due to long cross-linking reaction times and inability to quench this reaction at a defined time. Occasionally the stability of components is of concern and some components are rather expensive. For some formulations heavy metals are used as catalyst. It would therefore be advantageous to have a one component PDMS in hand that has a low viscosity of about 15000 cSt and cross-links at elevated temperatures. This could be achieved *via in-situ* polymerization of pure monomers. Polymer films prepared directly by *in-situ* polymerization are known in the literature⁹ as are silicone gels prepared directly from monomers.¹⁰ However, no detailed description of the

mechanical properties of the prepared materials was given. Additionally, thin silicone film formation for DEA by *in-situ* polymerization was not explored so far despite its potential.

This manuscript describes a new approach of preparing thin silicone films in the range of 100 to 200 μm for DEA starting directly from monomers. After a pre-polymerization step, when the monomers are converted to a low molar mass oligomer of low viscosity, thin films are formed by doctor blade technique, followed by curing of the oligomers to a solid elastic state. The mechanical as well as electromechanical properties of the resulting films are determined by tensile and circular actuator tests. They are systematically tuned in wide ranges by varying the amount of CL co-monomer used.

2. Experimental Section

2.1. Materials and Methods

Octamethylcyclotetrasiloxane (D_4), heptamethylcyclotetrasiloxane (D_4H), Karstedt's catalyst, methyltrivinylsilane were purchased from ABCR, tetramethylammonium hydroxide (TMAH), tetrabutylphosphonium hydroxide (TBPH), and benzoyl peroxide (BP) were purchased from Aldrich and used as received.

^1H NMR spectra were recorded with a Bruker Avance-400 spectrometer (^1H : 400 MHz at room temperature with CDCl_3 as solvent). MS spectra were obtained on a Bruker Autoflex using electron impact ionization (EI). The thermogravimetric analysis (TGA) was conducted with a Perkin Elmer TGA7 at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ under oxygen from 30 to $900\text{ }^\circ\text{C}$. The GC-MS investigations were done with an Agilent 5973 MS and 6890 GC column: BGB wax ($15\text{ m} \times 0.25\text{ mm} \times 0.5\text{ }\mu\text{m}$); split injection (1:30) at $250\text{ }^\circ\text{C}$; flow 1.5 ml/min , temperature gradient: $20\text{ }^\circ\text{C/min}$ after 1 min initial time at $50\text{ }^\circ\text{C}$.

The tensile tests were performed using a Zwick Z010 tensile test machine with a crosshead

speed of 500 mm/min. Tensile test specimens with a gauge width of 3 mm and a gauge length of 30 mm were prepared by die cutting. The strain was determined by a Zwick video extensometer 066975. The curves were averaged from 3 to 5 independent experiments. The tensile modulus was determined from the slope of the stress-strain curves using a linear fit to the data points within 10% strain.

The electromechanical tests were performed using circular membrane actuators, for which the films were fixed between two circular frames. Circular electrodes (8 mm diameter) of carbon black powder were applied to each side of the film. A FUG HCL-35-12500 high voltage source served as power supply for actuator tests. The voltage was increased by 100 V every 2 s up to breakdown. The actuation strain was measured optically as the extension of the diameter of the electrode area via a digital camera, using an edge detection tool of a LabView program to detect the boundary between the black electrode area and the transparent silicone film.

2.2. Preparation of Monomers

1,2-bis-heptamethylcyclotetrasiloxanyl-ethane (CL₁) solution in D₄

To degassed D₄ (50 g, 0.17 mol) heated to 120 °C, a solution of BP (1 g, 4 mmol) dissolved in benzene (6 ml) was added dropwise under Ar. The reaction mixture was let at this temperature for 1 h and then the residue was purified by filtration over a short column of silica gel. The product was washed out of column by using hexane to give a solution of 1,2-bis-heptamethylcyclotetrasiloxanyl-ethane in D₄. The solvent was removed and the product was analyzed by gas chromatography and mass spectrometry in order to find the amount of CL contained. Depending of the amount of BP used the proportion of CL₁:D₄ was varied (Table 1).

Tris-(2-heptamethylcyclotetrasiloxane-yl-ethyl)-methylsilane (CL₂)

CL₂ was prepared according to the literature.¹¹ Briefly: to a solution of D₄H (0.50 g, 0.52 ml, 1.77 mmol) in 5 ml toluene, methyltrivinylsilane (0.07 g, 0.59 mmol) and platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (5 µl) were added. The reaction mixture was stirred at room temperature for 24 h, the solvent was removed and the resulting oil was filtrated over silica gel using hexane as eluent to give CL₃ as colorless oil. ¹H NMR shows the expected signals that are similar to the reported one (See Supporting Information).¹⁵ MALDI-TOF (matrix: α-Cyano-4-hydroxycinnamic acid): ¹H NMR (400 MHz, CDCl₃, δ): -0.07, -0.02, 0.09 (3 s, 66 H), 0.59-0.34 (m, 10.1 H), 1.01 (d, 1.27 H); ¹³C NMR (60 MHz, CDCl₃, δ): -6.69, -5.99, -1.62, -1.57, 0.37, 0.82, 0.80, 0.77, 0.76, 3.72, 3.81, 4.17, 5.58, 8.44, 9.05, 9.21, 9.22; 1143.3 [M+matrix-CH₃], 955.2 [M-CH₃]; GPC (THF): *M_n* = 1140, *M_w* = 1150 g/mol, *M_w*/*M_n* = 1; Anal. calcd. for C₂₈H₇₈O₁₂Si₁₃: C 34.60, H 8.09; found: C 34.80, H 7.83.

2.3. Thin Film Formation

Thin Film Formation from CL₁ solution in D₄

To 50 ml of the above purified solution, TMAH (0.01 g) was added and heated to 110 °C under argon. An increase in the viscosity was observed. Care must be taken that the reaction is not done to completion, but rather stopped when the desired viscosity is achieved (typically between 5 to 10 min). Thin films are formed by doctor blade and the films are cross-linked to a solid elastic state by heating to 110 °C followed by heating to 140 °C to decompose the initiator. If the pre-polymerization is performed at temperatures lower than 110 °C, the increase in viscosity is slowed down.

General Procedure for the Film Formation using CL₂

To D₄ (4 ml, 3.82 g, 13 mmol), TMAH (0.005 g) was added under argon at 110°C and stirred at this temperature until the viscosity is increased. The reaction was cooled to room

temperature and then CL₂ was added. For the amounts please see Table 2. Cross-linked films were made as described above.

To verify the stability of our formulation after addition of CL at room temperature, the formulation was let to equilibrate. The equilibration process was followed by ¹H NMR spectroscopy. After 5 day, no further change was observed. Cross-linking of the equilibrated mixture allowed formation of elastomers with similar characteristics as the one above.

3. Results and Discussion

3.1. Synthesis of Monomers that Act as Cross-Linkers

As mentioned in the introduction, silicone elastomers with good elastic properties are normally made by cross-linking a high M_w PDMS. We propose here the synthesis of silicone elastomers by polymerization of D₄ in the presence of two functional co-monomers that act as CL (Scheme 1). A large variety of other co-monomers could in principle be used. For an overview of possible CL please see the work by Chang et al.¹¹

Scheme 1. Synthesis of functional monomers that act as CL: CL₁ from D₄ in the presence of BP; CL₂ from D₄H by hydrosilylation with methyltrivinylsilane.

1,2-Bis-heptamethylcyclotetrasiloxanyl-ethane (CL₁) was obtained as a solution in D₄, by reacting D₄ with BP (Scheme 1).¹² To remove the unreacted peroxide, the acids and esters that formed during the reaction, a short silica gel column was used. Further attempts to separate CL₁ from D₄ were not successful and therefore the purified reaction mixture was used as such to make thin films. It was reported that the concentration of CL₁ in D₄ can be tuned by using different amounts of peroxide.¹³ We systematically increased the amount of BP used while keeping the amount of D₄ constant and expected an increase of the concentration of CL₁ in D₄

(Table 1). The reaction mixtures were analysed by a gas chromatograph (GC) coupled to a mass spectrometer (MS). However, no systematic increase in the relative concentration of CL₁ in D₄ with increasing amount of peroxide used was observed (see Table 1). In GC, D₄ was detected at a retention time of 3.3 min, a small contamination of D₄ by pentamethylcyclotrisiloxane was detected at 3.4 min, while at 7.3 min, CL₁ was detected. The structure of CL₁ was supported by the mass spectrum that shows the molecular ion minus a methyl group [M-CH₃]⁺ at $m/z = 575$, which is a common fragmentation process for methylsiloxane.

Table 1.

CL₂ was prepared by hydrosilylation of D₄H with methyltrivinylsilane. The product was purified by column chromatography over silica gel. The disappearance of the typical Si-H signal of D₄H at 4.7 ppm and the signal of the olefinic protons of methyltrivinylsilane is a clear indication for coupling (See Supporting Information). The disappearance of Si-H band at 2155 cm⁻¹ was also confirmed by FT-IR spectroscopy. Additionally, the MALDI-TOF mass spectrum of CL₂ shows the expected molecular ion minus a methyl group at $m/z = 955.2$. The GPC shows only one single peak with $M_w = 1140$ g/mol ($PDI = 1$) and confirms that all three vinyl groups are reacted. A mixture of Markovnikov and *anti*-Markovnikov products formed made the interpretation of the ¹H NMR challenging (See Supporting Information).

3.2. Film Formation and Characterization

PDMS are easily prepared starting from D₄ or hexamethylcyclotrisiloxane (D₃) monomers under anionic or cationic conditions.¹⁴ We focused on anionic polymerization because it

allows a good control over the molar mass. Strong bases like alkali metal hydroxides are often used as initiators. They however, must be removed since they are still active and cause depolymerization at elevated temperatures.¹⁵ For the polymerization TMAH was selected because it decomposes above the polymerization temperature to inactive products (Scheme 2).¹⁶

Scheme 2. Synthesis of silicone elastomer films from D₄ and CL in the presence of TMAH. The initiator decomposes to inactive components at elevated temperatures.

Two series of materials were prepared: materials **A** with CL₁ and materials **B** with CL₂. Table 2 summarises the prepared materials using different types of CL and different amounts of base, as well as the elastic moduli at different strain and elongations at break. Materials **A** were prepared starting from solutions of CL₁ of different concentrations in D₄ by polymerization using different amounts of TMAH base. Thus, a solution of CL₁ in D₄ was pre-polymerized first to a liquid of desired viscosity. The reaction mixture was then coated on a Teflon substrate by using doctor blade technique. The resulting film was fully polymerized to a highly transparent elastomer at 110°C. To increase its stability, the initiator was decomposed by heating to 140°C.

All prepared materials (**A1**, **A2**, **A3**, **A4**) allowed preparation of thin films of high quality and excellent elastomeric properties with strain at breaks as high as 540 % (Figure 2, Table 2). It is known that the mechanical properties of an elastomer are dependent on the cross-linking density. The cross-link density was tuned by either varying the amount of BP used for CL₁ synthesis in D₄ solution or by the amount of TMAH used (Table 1). For example, by keeping the amount of BP constant and increasing the amount of TMAH, an increase in elastic moduli at all strains was observed (Entry **A1** and **A2**). When the amount of base was however kept constant and the amount of BP used was reduced, a decrease in the elastic moduli at all strains

was observed (Entry **A2** and **A3**). This is most likely due to an increase in the cross-linking density due to the increase of CL₁ concentration in material.

Figure 2. Stress strain curves of the films prepared with different bases and different amounts of BP.

Table 2.

As mentioned before, CL₁ was prepared as a solution in D₄ by using a free radical reaction. It was observed that it is rather difficult to precisely control the concentration of CL₁ in D₄ since free radical reactions are rather difficult to control. We therefore decided to explore the synthesis of other materials where the CL concentration is precisely controlled. Cross-linker CL₂ was prepared as described above and isolated in pure form. With this cross-linker materials of series **B** were prepared (Table 2). The polymerization of D₄ with different amounts of CL₂ and TMAH allowed formation of films with tunable mechanical properties (Figure 3). The amount of TMAH was kept to 5 mg per 4 g D₄ since this amount should give high molecular weight PDMS chains which would ensure materials with good elastic properties. Three materials with different elastic properties were easily prepared just by using different concentrations of CL₂ (Table 2). A decrease in the elastic moduli at 100% strain from 1370 kPa to 424 kPa was observed by decreasing the amount of CL₂ by a factor 4 (Table 1). The tensile tests were made shortly after the materials had been cross-linked and also after more than half a year after preparation. The stress strain curves were superimposable, which indicates that the aging of these materials does virtually not affect their mechanical properties.

Figure 3. Stress–strain curves for the silicone films prepared from D₄ and different amount of CL₂ from standard tensile tests at 500 mm min⁻¹.

Materials **B** were submitted to a swelling/extraction procedure in order to determine the amount of non-bonded species as well as the network density. The cross-linked PDMS materials were extracted by immersion in toluene for several days at room temperature,¹⁷ whereby the solvent was replaced for fresh one every 24 h. The materials were then let drying to constant mass. They were weighted before (m_0) and after extraction (m_1) and the extractable fraction was calculated according to:

$$W_{ext}(\%) = (m_0 - m_1)/m_0 \times 100$$

The amount of extractable material was less than 7% (Table 3).

The most important parameters for characterizing an elastomer is the average molecular weight between cross-links M_c ($M_c = 1/2\eta$) and the network density η which gives the concentration of net points per volume.¹⁸ By using the Flory-Rehner equation, it is possible to estimate the density of the polymer network from the swelling degree supposed the Flory solvent-polymer interaction parameter χ is known (**Table 3**).

$$\eta_{swell} = \frac{-\ln(1 - V_r) - V_r - \chi V_r^2}{2V_s(V_r^{1/3} - 2V_r/f)}$$

V_s is the molar volume of the solvent (toluene)

η_{swell} is the number of effective network chains/cm³ of rubber (cross-link density),

f is the functionality of cross-link.

The values of χ and f were obtained from the literature,¹⁹ whereas V_r (the volume fraction of silicone rubber) was calculated from:

$$V_r = \frac{(m_1/\rho_1)}{(m_1/\rho_1) + (m_2/\rho_2)}$$

m_1 and m_2 are the weights of the polymer samples and the solvent taken from the swelling/extraction tests, and ρ_1 and ρ_2 are the densities of the silicone and of toluene, respectively.

As expected, the network density η decreases from 19.7×10^{-5} mole/cm³ for material **B1** to 4.79×10^{-5} mole/cm³ for material **B3** with decreasing amount of CL used. Both η values are however higher than expected, based on the concentration of CL in D₄ used for the entire cross-linked formulations investigated. This is most likely due to entanglements of the polymer chains and also due to evaporation of some unreacted cyclic compounds during TMAH decomposition (typically about 20 %). The decrease in the moduli of elasticity for materials **B** with decreasing LC is in good agreement with the decrease in network density.

Table 3.

Cyclic tests were performed with **B2** to evaluate the mechanical fatigue resistance (Figure 4). The sample was strained from 0 % to 100 % strain at a rate of 20 mm/min. The stationary time at maximum strain was 2 min, while stationary time at minimum strain was 1 min. The tests proved the elastic behaviour of our elastomer, with a clearly visible hysteresis loop only at the first strain-release cycle and negligible difference between cycles. The area within the loop is directly correlated to the viscoelasticity of the material.

Figure 4. Cyclic stress-strain mechanical tests.

Materials **B** were also investigated regarding their thermal stability. TGAs run under an oxygen flow, show that the materials are stable up to 200 °C where the first decomposition step was observed (about 3%). This step is most likely due to some residual monomers left in the material. Two other decomposition steps were observed at about 360 °C and one above 500 °C (Figure 5). It is known that the silicone-carbon bond can withstand 600 °C but temperatures of 250 to 360 °C are the limit for silicone-oxygen bonds. Therefore, it is reasonable to assume that the degradation with maximum at 360 °C is due to evaporation of

some cyclic compounds that are formed through the equilibrium between cyclics and polymer structure. This equilibrium is shifted to the cyclics at elevated temperatures. After these steps, less than half of the material is left, which is typical for silicone elastomers that are degraded in presence of oxygen. The residue is most likely some highly cross-linked material and silica. The slight decrease in thermal behavior of the silicones presented here is most likely due to the hydroxyl end-groups which are present in the material (water was used as end-blocker). It has been shown that such groups can reduce the thermal degradation of silicones.²⁰

Figure 5. TGA thermograms of **B** heated at a rate of 20 ° min⁻¹ in oxygen flow.

3.3. Electromechanical properties

Although the main focus of this research was to develop alternative routes to silicone elastomers with tunable mechanical properties, due to the good properties of the resulting films, we decided to further explore the possibility of using these materials in DEA. Up to now, all materials used in commercial DEA products are based on silicone.²¹ Such silicone films are made by vinyl-addition cure between a silyl hydride and a vinyl group catalyzed by a platinum complex. This cross-linking is effective and allows preparation of elastomers with a high level of network control. It can be done without solvent and no by-products are formed during cross-linking. To finish the cross-linking however, a postcure thermolysis is used. Formulations are made of two components: one contains a PDMS that carry vinyl groups and the other is a PDMS that has silyl hydride groups and the catalyst. Several drawbacks were noted with such formulations. For example, after the two components are mixed, limited amount of time is left for processing because the cross-linking reaction starts already at room temperature. This reaction is sensitive to impurities which can poison the catalyst rendering control difficult. Another disadvantage of these formulations is the high cost of the Pt catalyst, despite of the low concentration used, and the contamination of the final product with it.

Residual Pt in silicone network hinders applications e.g. in biomedical products. Of concern is also the stability of components against hydrolysis and oxidation which has a direct impact on the pot lifetime.

Herein, a one component PDMS formulation with good pot lifetime was developed. Its viscosity can be easily controlled by the time and the temperature of reaction used for the pre-polymerization. The mechanical properties can be adjusted by the concentration of CL co-monomer used. Low viscosity formulations allowed coating and cross-linking on substrates, while the more viscous formulations could be used in combination with injection molding or extruding. The mechanical properties of the resulting films do not alter in time. Therefore, these formulations are of great interest as dielectricum for actuator.

As next, the electromechanical properties of selected materials were investigated in actuators test. The determined actuation strains are shown in Figure 6 as a function of nominal electric field strength. Both materials **A** and **B** allowed construction of actuators that showed high breakdown fields of 37 V/ μm . Actuators from material **A** were measured at two different pre-strains. It was observed that the lateral actuation strain at the same field increases from 5% for an actuator that was 30% pre-strained to 20 % for an actuator that was 40 % pre-strained, respectively.

Materials **B** allowed construction of actuators with even higher breakdown fields then material **A** (Figure 6). For materials **B1** and **B2** a breakdown field of 57 V/ μm was measured, while **B3** had a breakdown of 48 V/ μm . It should be mentioned here, that the breakdown experiments were conducted with a setup similar to that described by Kollosche et al. and 10 samples were measured and the data were averaged.²²

Figure 6. Lateral actuation strain of membrane actuators for different silicone films as a function of the applied voltage.

For materials **B2** and **B3** the actuation strain was almost the same except that the breakdown field for material **B2** was higher. The increase in the breakdown for **B2** compare to **B3** is most likely due to it higher moduli of elasticity. The maximum actuation strain for **B2** was 4.3% at 43 V/ μm . Actuator measurements of material **B1** were not possible since the material did not withstand 30% pre-strain used for construction of actuators.

The performance of **B2** was further investigated regarding its long-term stability under high voltages (Figure 7). The actuator was activated with a sinusoidal voltage with a peak value of 5000 V (38 V/ μm) at 10 Hz (leading to a 5 Hz actuation response). After more than 10000 cycles no degradation was observed.

These results clearly show that such films are stable under the applied electric field and can be used for a large number of cycles even at voltages close to the breakdown strength.

Figure 7. Long term stability of **B2** at 5 Hz and 5000 V (38 V/ μm). No degradation was observed after 10000 cycles.

The possibility of using these materials in combination with high permittivity fillers to further improve the actuation strain is under investigation.

4. Conclusions

We showed that it is possible to prepare thin silicone films with good mechanical and electromechanical properties by *in-situ* polymerization of specially designed monomers. The mechanical properties are easily tuned by altering the amount of CL used. Materials with strain at break as high as 800% were prepared despite of the fact that no silica filler is used for reinforcement. The materials are stable up to a temperature of 200 °C and the amount of extractable oligomers is very low (< 7%). Additionally, the mechanical properties do not alter

in time and can withstand high electric fields which make them attractive for dielectric elastomer actuator application. This procedure can be extended to other silicone monomers and CL and suggests a broad applicability of the method. Our elastomers can be used not only as dielectricum in actuators, but also as sealant material. Additionally, the application of these materials in electrically tunable lenses should not be underestimated.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author ((delete if necessary))

Appendix/Nomenclature/Abbreviations

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Figure 1. Cross-section of the non-activated (left) and the activated states of a dielectric elastomer actuator (right).

Figure 2. Stress strain curves of the films prepared with different bases and different amounts of BP.

Figure 3. Stress–strain curves for the silicone films prepared from D₄ and different amount of CL₂ from standard tensile tests at 500 mm min⁻¹.

Figure 4. Cyclic stress-strain mechanical tests for **B2**.

Figure 5. TGA thermograms of materials **B** heated at a rate of $20\text{ }^{\circ}\text{ min}^{-1}$ in oxygen flow.

Figure 6. Lateral actuation strain of membrane actuators for different silicone films as a function of the applied voltage.

Figure 7. Long term stability of **B2** at 5 Hz and 5000 V (38 V/μm). No degradation was observed after 10000 cycles.

Scheme 1. Synthesis of functional monomers that act as CL: CL₁ from D₄ in the presence of BP and CL₂ from D₄H by hydrosilylation with methyltrivinylsilane.

Scheme 2. Synthesis of silicone elastomer films from D₄ and CL in the presence of TMAH. The initiator decomposes to inactive components at elevated temperatures.

Table 1. Samples prepared from D₄ (50 ml) and BP as well as the signal intensities of the CL₁ determined from the reaction mixture by GC-MS.

Entry	BP (g)	[CL ₁] (counts)	[D ₄] (counts)	CL ₁ :D ₄
1	0.5	30×10 ³	150×10 ⁶	0.13×10 ⁻³
2	1	400×10 ³	84×10 ⁶	4.8×10 ⁻³
3	2	300×10 ³	52×10 ⁶	5.8×10 ⁻³
4	3	190×10 ³	44×10 ⁶	4.3×10 ⁻³
5	4	160×10 ³	47×10 ⁶	3.4×10 ⁻³

Table 2. Silicones prepared starting from D₄ and different amount and type of CL and base, the corresponding elastic moduli at different strain levels as well as the elongation at break.

Entry	CL	CL[μ l]/ D ₄ [ml]	Base	Y _{1%} [kPa]	Y _{20%} [kPa]	Y _{50%} [kPa]	Y _{100%} [kPa]	Elong. [%]
A1	CL ₁	3 ^{a)}	2 mg ^{b)}	207	143	101	73	539
A2	CL ₁	3 ^{a)}	5 mg ^{b)}	665	554	323	208	427
A3	CL ₁	2 ^{a)}	5 mg ^{b)}	618	456	269	182	452
A4	CL ₁	0.5 ^{a)}	8 mg ^{b)}	266	192	111	642	532
B1	CL ₂	100/4	5 mg ^{b)}	1973	1525	1094	1174	186
B2	CL ₂	50/4	5 mg ^{b)}	815	614	366	291	305
B3	CL ₂	25/4	5 mg ^{b)}	689	511	345	214	606

Type of initiator used: ^{a)}amount of BP used to D₄ (50 ml) and ^{b)}amount of TMAH base used for 4 g D₄.

Table 3. The percentage of extractable species (W_{ext}) and the cross-link densities obtained from swelling/extraction tests using the Flory-Rehner method for PDMS materials prepared with different amount of cross-linker.

Sample	W_{ext} (%)	η (mole/cm ³)	M_c
B1	6.6	19.7×10^{-5}	2540
B2	4.8	13.2×10^{-5}	3775
B3	6.4	4.79×10^{-5}	10440

The table of contents entry

Thin silicone films with good mechanical and electromechanical properties were prepared by *in-situ* polymerization of monomers. Octamethylcyclotetrasiloxane and specially designed co-monomers that function as cross-linkers were pre-polymerized to a liquid of low viscosity. This liquid is used to make thin films which are then fully polymerized to a highly transparent, cross-linked elastomer.

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Soft Polydimethylsiloxane Thin Elastomeric Films by In-situ Polymerization to Be Used as Dielectricum in Actuators

ToC figure

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Supporting Information

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Soft Polydimethylsiloxane Thin Elastomeric Films by In-situ Polymerization to Be Used as Dielectricum in Actuators

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Figure 1 (SI). ^1H NMR spectra of CL_2 (Markovnikov and anti-Markovnikov products top) and the two starting materials (middle and bottom)

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 APCI(+) MeCN_water
 CIM41_300_4000_FT_121221161759 #1-15 RT: 0.02-0.63 AV: 15 NL: 4.62E5
 T: FTMS + p MALDI Full ms [300.00-4000.00]

Figure 2 (SI). MS spectrum of CL₂

Figure 3 (SI). TGA thermograms of **B** heated at a rate of 20°C min⁻¹ in a helium flow.