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# Self-healable, high-permittivity elastomers for dielectric elastomer actuators

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## ABSTRACT

Polar group-modified polysiloxanes obtained by anionic ring-opening polymerization possess high dielectric permittivity and are of great interest for application in dielectric elastomer actuators (DEAs). A self-healing elastomer can be obtained by in situ polymerization and cross-linking using a cyclic siloxane monomer with polar side groups and a cross-linker consisting of multiple connected siloxane rings. In previous works, a non-polar cross-linker has been used, which requires the addition of a solvent for compatibilization with the polar monomer. In polymerization reactions of siloxanes, the addition of solvent leads to a more pronounced formation of cyclic by-products. These cycles impair the mechanical properties of the elastomer and cannot be removed after the reaction, as the material is already cross-linked. Therefore, in this work, we use a polar cross-linker that can be mixed with the polar monomer without adding solvent. Nitrile groups have been studied extensively for increasing the permittivity of the polysiloxane backbone. For a functionalization of 100%, a dielectric permittivity of ~18 was reached. In most cases, the nitrile group was attached to the siloxane backbone in the form of cyanopropyl groups. Still, the influence of the alkyl spacer on the material's dielectric and mechanical properties has not been studied. In this work, we synthesize cyanoalkyl-functional cyclic siloxanes with different lengths of the alkyl spacer and polymerize them solvent-free to high-permittivity polysiloxanes.

**Keywords:** high-permittivity elastomers, dielectric elastomers, soft actuators, self-healing, recycling, soft robotics.

## 1. INTRODUCTION

Dielectric elastomer actuators (DEAs) are a class of soft transducers that transform an electrical stimulus into mechanical work.<sup>1-3</sup> Due to their fast response and the well-controllable electrical stimulation, they have a high potential for applications in soft robotics and artificial muscles.<sup>4</sup> However, the major drawback of DEAs is the high operating voltage in kilovolts range.<sup>5</sup> One promising approach to decrease the driving voltage is increasing the dielectric elastomer's relative permittivity.<sup>6</sup> This can be achieved by introducing polar side groups to the polymer backbone and thus increasing the material's polarizability.<sup>7-12</sup> From the large number of different side groups that have been tested, nitrile groups stand out with a large increase in permittivity and high stability under ambient conditions.<sup>13</sup>

Just like natural muscles, DEAs are exposed to the risk of damage. In DEAs, damage can occur by mechanical stress or dielectric breakdown.<sup>14</sup> The risk for dielectric breakdown is especially high, given the large electric fields that need to be applied across the electrodes for actuation. In the case of a breakdown, the high current flow through the elastomer can lead to the burning of the device.<sup>15</sup> In order to increase the lifetime of DEAs, it is very attractive to employ self-healing materials that can recover from the different possible damages. As recently shown, one example of such self-healing, high-permittivity elastomers are nitrile group-modified polysiloxanes synthesized by anionic ring-opening polymerization.<sup>16</sup> They can be obtained by in situ polymerization and cross-linking using a cyclic siloxane monomer with cyanopropyl side groups and a cross-linker consisting of multiple connected siloxane rings (Figure 1). The reaction is initiated by anionic initiators such as tetrabutylphosphonium hydroxide (TBPH) or tetramethylammonium hydroxide (TMAH). After the polymerization, the ionic initiator and the silanolate end groups remain active in the product and are responsible for the self-healing properties. The silanolate end groups can initiate chain cleavage through backbiting at elevated temperatures. Consequently, the material reversibly softens upon heating and can self-heal after damage. The polar cyanopropyl groups increase the reactivity, which leads to faster self-healing than PDMS-based systems.<sup>17</sup>

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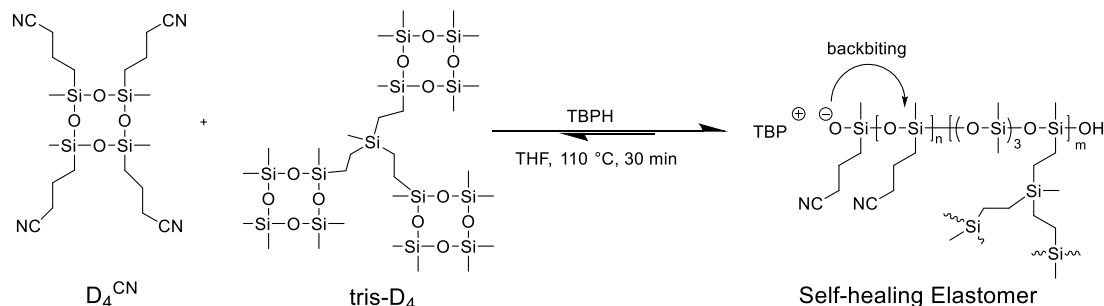


Figure 1: Previously reported synthesis of thermoreversible, high-permittivity elastomers by AROP starting from cyclic monomer  $\text{D}_4^{\text{CN}}$  and trifunctional cross-linker tris- $\text{D}_4$ .<sup>16</sup>

An elastomer with 7.5 wt% cross-linker was proven to heal within 10 min when heated to 80 °C (Figure 2). Repeated tensile tests also showed that the material could be completely reshaped by melt pressing three times, while only slightly impairing the mechanical properties.

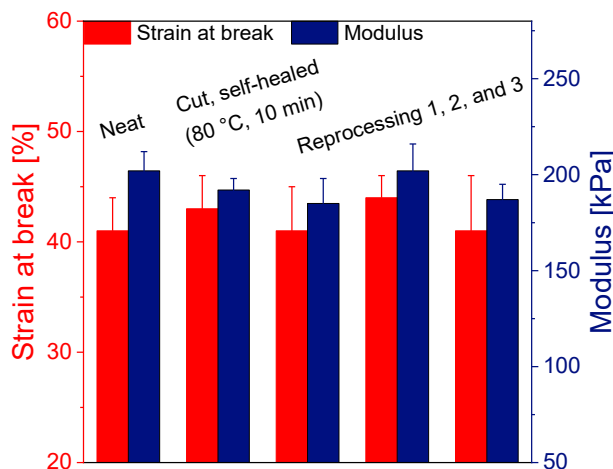


Figure 2: Self-healing experiments of one elastomer with 7.5 wt% cross-linker. The initial mechanical properties are restored after cutting and heating to 80 °C for 10 min. Also, the mechanical properties are only slightly impaired by up to three processing cycles.<sup>16</sup>

Despite the good results for self-healing and mechanical properties, the previously reported synthetic route also inhibits a major drawback. Due to the combination of polar monomer and non-polar cross-linker, solvent needed to be added during the polymerization reaction. The presence of solvent leads to an increased formation of cyclic by-products in the ring-opening polymerization.<sup>18</sup> These cycles have a negative impact on the mechanical properties and cannot be removed after the reaction, as the material is already cross-linked. Therefore, it is attractive to use a polar cross-linker, which can be mixed with the polar monomer without adding solvent.

Nitrile groups have been shown to be suitable polar side groups for increasing the permittivity of polysiloxanes.<sup>13,19–21</sup> A dielectric permittivity of around 18 is reached for 100% functionalization with nitrile groups.<sup>13</sup> In previous work, the nitrile group was attached to the silicone backbone in the form of cyanopropyl groups. So far, the influence of the propyl group on the material's dielectric and mechanical properties has not been studied. In this work, we synthesized four cyanoalkyl-functional cyclic siloxanes with cyanoethyl, cyanopropyl, cyanobutyl, and cyanopentyl side groups. In the next step, we polymerized and cross-linked them to elastomers having 2 to 5  $\text{CH}_2$  groups between the nitrile group and the silicone backbone. For the cross-linking, we used a polar, bifunctional cross-linker, which allowed us to perform the reaction solvent-free. We characterized the elastomers with respect to their dielectric and thermal properties to find the most promising candidate for the application in DEAs.

## 2. EXPERIMENTAL PART

### 2.1 Materials

Unless otherwise stated, all chemicals were reagent grade and used without further purification. Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene, Pt $\approx$ 2%), 2,4,6,8-tetramethylcyclotetrasiloxane (D<sub>4</sub>H<sub>4</sub>), divinyl dimethylsilane, 4-pentene nitrile, 5-hexene nitrile, and (2-cyanoethyl)methyldichlorosilane were purchased from ABCR. Allyl cyanide, TMAH (solution, 25 wt % in water), and anhydrous tetrahydrofuran were purchased from Aldrich. Sodium hydrogencarbonate, toluene, heptane, ethylacetate, and anhydrous toluene were purchased from VWR. (3-Cyanopropyl)methyldichlorosilane was purchased from Gelest. O-xylol was purchased from Merck.

### 2.2 Characterization

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded at 298 K on a *Bruker Avance* 400 MHz NMR spectrometer. Chemical shifts ( $\delta$ ) are given in ppm relative to CHCl<sub>3</sub> ( $\delta$  = 7.26 ppm for <sup>1</sup>H and  $\delta$  = 77.16 ppm for <sup>13</sup>C). Tensile tests were performed on a *Zwick Z010* tensile test machine at a crosshead speed of 500 mm min<sup>-1</sup> with a pre-load of 2 g. Test specimens with a gauge width of 2 mm and a gauge length of 18 mm were prepared by die-cutting. The stress-strain curves were averaged from at least five independent measurements. Impedance measurements were performed in a frequency range of 0.1 Hz – 1 MHz with a *Novocontrol Technologies* Alpha-A Frequency Analyzer. The root mean square voltage of the probing AC electric signal applied to the sample was 1 V. Differential scanning calorimetry was performed on a *Perkin Elmer* double-furnace DSC 8000 with a heating rate of 20 K min<sup>-1</sup>.

### 2.3 Synthesis of the polar monomers and the polar cross-linker

**Synthesis of 1,3,5,7-tetra(2-cyanoethyl)cyclotetrasiloxane (D<sub>4</sub>-2-CN):** In a 500 mL two-necked flask equipped with a magnetic stirrer, dropping funnel, dean-stark trap, and azeotropic condenser, NaHCO<sub>3</sub> (29.40 g, 350 mmol) is dispersed in toluene (120 mL). 2-Cyanoethylmethyldichlorosilane (14.0 mL, 100 mmol) is dissolved in dry toluene (30 mL) and added dropwise to the dispersion at RT. The evolving CO<sub>2</sub> is led into a water bath. After the addition, the mixture is stirred at 110 °C for 3 h and the water is removed by azeotropic distillation. The reaction mixture is filtered and washed with toluene. The organic phase is washed with water twice. Toluene is removed in vacuo and the product is dried in HV. Yield: 10.37 g (91.6%) of colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.51–2.35 (m, 8H), 1.08–0.94 (m, 8H), 0.35–0.21 ppm (m, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ): 120.57, 12.69, 11.00, -0.57 ppm.

**Synthesis of 1,3,5,7-tetra(3-cyanopropyl)cyclotetrasiloxane (D<sub>4</sub>-3-CN):** In a 500 mL two-necked flask equipped with a magnetic stirrer, dropping funnel, dean-stark trap, and azeotropic condenser, NaHCO<sub>3</sub> (29.40 g, 350 mmol) is dispersed in toluene (120 mL). 3-Cyanopropylmethyldichlorosilane (15.8 mL, 100 mmol) is dissolved in dry toluene (30 mL) and added dropwise to the dispersion at RT. The evolving CO<sub>2</sub> is led into a water bath. After the addition, the mixture is stirred at 120 °C for 1 h and at 110 °C for 3 h and the water is removed by azeotropic distillation. The reaction mixture is filtered and washed with toluene. The organic phase is washed with water three times. Toluene is removed in vacuo and the product is dried in HV. Yield: 8.67 g (68.2%) of colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.47–2.33 (m, 1H), 1.80–1.64 (m, 1H), 0.83–0.66 (m, 1H), 0.22–0.11 ppm (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ): 119.76, 20.19, 19.61, 19.25, 16.45, -0.54 ppm.

**Synthesis of 1,3,5,7-tetra(3-cyanobutyl)cyclotetrasiloxane (D<sub>4</sub>-4-CN):** A dried 500 mL 3-necked flask equipped with a reflux condenser and a magnetic stirrer is put under argon. Tetramethylcyclotetrasiloxane (2.44 mL, 10 mmol) is added and dissolved in dry toluene (5 mL). 4-Pentene nitrile (5.0 mL, 50 mmol) and Karstedt's catalyst (18  $\mu$ L) are added via a syringe. The solution is heated to 110 °C and stirred under reflux for 5 days. The reaction progress is followed by NMR spectroscopy. After 4.5 days, 5 days, and 5.5 days another 18  $\mu$ L catalyst is added to the reaction mixture. After 6 days, the solvent is removed in vacuo. The product is purified by silica gel filtration (heptane/EtOAc 1:1). The solvents are removed and the product is dried in HV. Yield: 2.46 g (43.5%) of yellowish oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 2.43–2.34 (m, 6H), 1.76–1.64 (m, 7H), 1.60–1.45 (m, 6H), 0.67–0.54 (m, 6H), 0.25–0.10 ppm (m, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ): 119.69, 28.69, 22.17, 16.81, 1.02 ppm.

Synthesis of 1,3,5,7-tetra(3-cyanopentyl)cyclotetrasiloxane (**D4-5-CN**): A dried 50 mL 3-necked flask equipped with a reflux condenser and a magnetic stirrer is put under argon. Tetramethylcyclotetrasiloxane (2.07 mL, 8.5 mmol) is added and dissolved in dry toluene (5 mL). 5-Hexene nitrile (5.0 mL, 42.5 mmol) and Karstedt's catalyst (18  $\mu$ L) are added via a syringe. The solution is heated to 110 °C and stirred under reflux for 5 days. The reaction progress is followed by NMR spectroscopy. After 1.5 days, 4.5 days, 5.0 days and 5.5 days, another 18  $\mu$ L catalyst is added to the reaction mixture. After 6 days, the solvent is removed in vacuo. The product is purified by silica gel filtration (heptane/EtOAc 1:1). The solvents are removed and the product is dried in HV. Yield: 2.55 g (48.4%) of yellowish oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 2.40–2.29 (m, 6H), 1.72–1.59 (m, 6H), 1.54–1.44 (m, 6H), 1.44–1.31 (m, 6H), 0.63–0.46 (m, 6H), 0.22–0.03 ppm (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 119.80, 31.93, 25.12, 22.20, 17.09, 1.00, -0.58 ppm.

Synthesis of the polar cross-linker (**PCL**): In a 500 mL three-neck flask equipped with a magnetic stirrer and a dropping funnel,  $\text{D}_4\text{H}_4$  (54 mL, 222.5 mmol) was dissolved in *o*-xylene (100 mL) and mixed for 5 min. Karstedt's catalyst (0.1 mL) and divinyltrimethylsilane (13.5 mL, 89 mmol) were dissolved in *o*-xylene (100 mL) and the mixture was slowly added to the  $\text{D}_4\text{H}_4$  solution. After addition, the reaction was stirred at RT for 24 h. Then, the excess  $\text{D}_4\text{H}_4$  was removed in vacuo. Allylcyanide (50.4 mL, 623 mmol) and Karstedt's catalyst (0.1 mL) were added to the reaction mixture and the mixture was stirred for 4 days at 110 °C under reflux. The solvent was removed in vacuo and the product was dried in HV.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 2.48–2.36 (m, 12H), 1.81–1.67 (m, 12H), 0.77–0.71 (m, 12H), 0.45 (m, 8H), 0.30–0.06 (m, 35H).

## 2.4 Synthesis of the high-permittivity elastomers (E2-E5)

The respective amounts of polar monomer and polar cross-linker are added in a 50 mL three-necked flask equipped with a magnetic stirrer. TMAH (0.92 mol% with respect to the polar monomer) is added as 25% solution in water and the mixture is dried in HV at RT for 30 min. Afterward, the flask is put under argon in a pre-heated oil bath at 110 °C and the mixture is stirred for 10 min. Then, the product is molded into one piece on the heating plate at  $\sim 90$  °C. Elastomer films were prepared from the crude product by melt pressing using a copper spacer with a thickness of 200  $\mu\text{m}$  between two PET sheets coated with PTFE foil. The arrangement was covered with metal plates on the top and bottom sides and placed inside a melt press at temperatures between 80 °C and 100 °C. After an equilibration time of 5 min, a pressure of 1000 kg was applied for 1 min. The resulting film was left to cool before removing it from the substrate.

## 3. RESULTS AND DISCUSSION

To obtain self-healing elastomers, we polymerized and cross-linked the polar monomers in one step by AROP with TMAH as initiator. Using a polar cross-linker allowed us to carry out the polymerization reaction solvent-free. The reaction scheme is shown in Figure 3. In the first step, we varied the concentration of polar, bifunctional cross-linker **PCL** to investigate the influence on the mechanical properties of the formed elastomers. Therefore we chose monomer **D4-3-CN** as a model compound, as it can be synthesized on a large scale by condensation reaction and the respective chlorosilane has the lowest price. Three elastomers, **E3A** to **E3C**, with cross-linker concentrations of 10 wt%, 15 wt%, and 20 wt% were synthesized (Table 1).

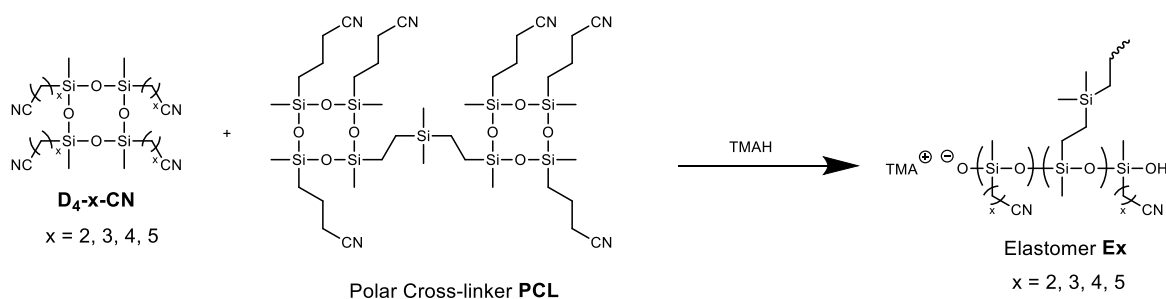


Figure 3: Synthesis of self-healing elastomers **Ex** by in-situ polymerization and cross-linking of monomers **D4-x-CN** with the polar, bifunctional cross-linker **PCL**, where x stands for the number of  $\text{CH}_2$  groups between the silicone backbone and the nitrile group.

A fourth reaction batch with a cross-linker concentration of 5 wt% did not cross-link properly, as the amount of cross-linker was too small for achieving a sufficient cross-linking density. The mechanical properties of the three elastomers were investigated by tensile testing (Figure 4a) and the results are summarized in Table 1. The strain at break decreases with increasing cross-linker concentration from  $119\pm 8\%$  for elastomer **E3A** to  $43\pm 5\%$  for elastomer **E3C**. At the same time, the Young's modulus increases from  $95\pm 7$  kPa to  $302\pm 49$  kPa.

Table 1: Amount of cross-linker and mechanical properties of the three elastomers obtained from the polymerization of monomer **D4-3-CN**.

Elastomer	Amount of PCL [wt%]	Strain at break [%]	Young's modulus [kPa]
<b>E3A</b>	10	$119\pm 8$	$95\pm 7$
<b>E3B</b>	15	$71\pm 6$	$165\pm 14$
<b>E3C</b>	20	$43\pm 5$	$302\pm 49$

For the application in DEAs, the dielectric elastomer needs to have a sufficient strain at break, a fairly low modulus, and a good elasticity with low viscous losses. Therefore, elastomer **E3B** shows the best combination of properties, as the viscous losses for elastomer **E3A** were already too large. Consequently, we polymerized the other polar monomers with a molar ratio of 7.7 mol% polar cross-linker with respect to the polar monomer. This corresponds to the same molar ratio that is reached for 15 wt% **PCL** in monomer **D4-3-CN**.

Polymerization of the monomers **D4-2-CN** to **D4-5-CN** yields elastomers **E2** to **E5**, which were characterized by DSC (Figure 4b) and dielectric impedance spectroscopy (Figure 5).

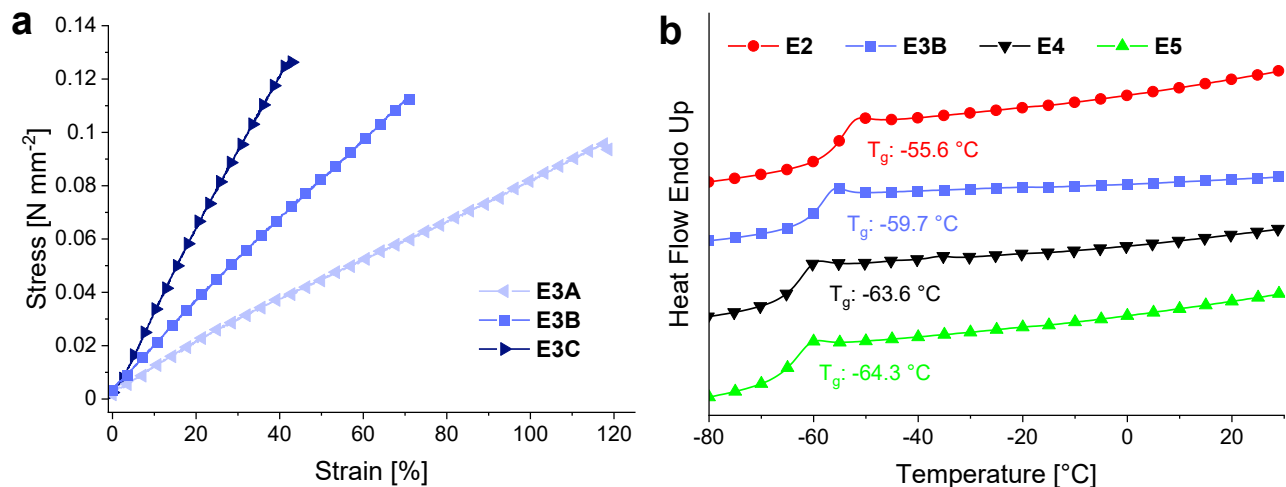


Figure 4: a) Tensile test curves of elastomers **E3A**, **E3B**, and **E3C** with different concentrations of polar cross-linker. b) DSC curves of the four elastomers with different cyanoalkyl side groups.

Dielectric impedance spectroscopy provides information about the dielectric properties of the elastomers. The results for conductivity ( $\sigma'$ ), dielectric loss tangent ( $\tan(\delta)$ ), dielectric loss ( $\epsilon''$ ), and relative permittivity ( $\epsilon'$ ) are plotted in Figure 5 as a function of frequency. All elastomers exhibit quite large values for the conductivity of up to  $10^{-6}$  S  $\text{cm}^{-1}$ , which is

likely caused by the ionic initiator TMAH. The permittivity shows a linear increase towards low frequencies due to electrode polarization. Here, mobile ionic residues accumulate at the electrodes leading to interfacial polarization. At high frequencies, the alignment of the polar side groups in the electric field determines the permittivity. The permittivity at  $10^6$  Hz of the four elastomers is given in Table 2. The permittivity increases with decreasing length of the alkyl spacer between the nitrile groups and the silicone backbone from  $11.4 \pm 0.2$  for elastomer **E5** to  $18.5 \pm 0.2$  for elastomer **E2**. This effect is caused by the increasing concentration of the nitrile dipoles, which contribute to the polarizability of the elastomer. The step in permittivity between elastomer **E3B** and **E2** of 0.4 is much smaller than the other elastomers. This can be explained by the lower mobility of the polymer chain segments for short alkyl spacers. The ability of the dipoles to align in the field is impaired by the interaction between the dipoles, which becomes more and more important with increasing dipole concentration. This effect almost outweighs the positive effect of the increased dipole concentration for elastomer **E2**.

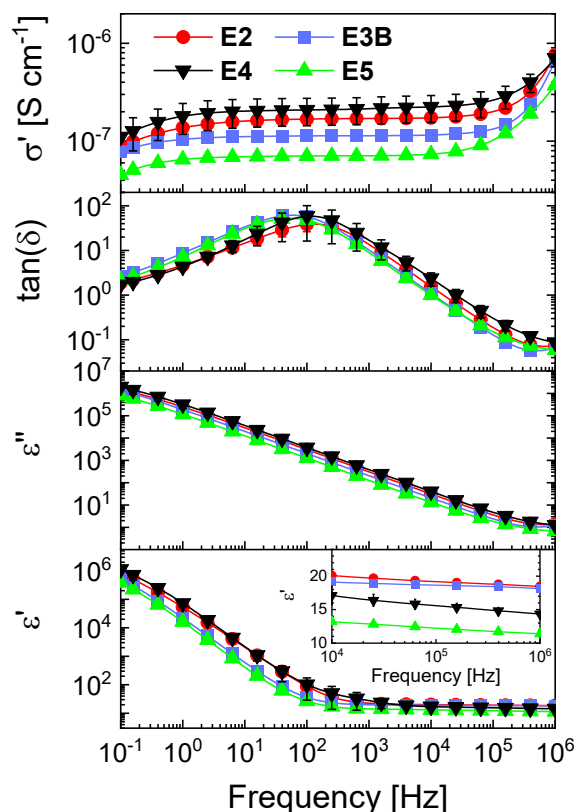


Figure 5: Conductivity ( $\sigma'$ ), dielectric loss tangent ( $\tan(\delta)$ ), dielectric loss ( $\epsilon''$ ), and permittivity ( $\epsilon'$ ) of the four elastomers with different cyanoalkyl side groups measured at RT as a function of frequency.

The decrease in polymer chain segment mobility with decreasing number of  $\text{CH}_2$  groups can also be observed by DSC. The  $T_g$  increases from  $-64.3$  °C for elastomer **E5** to  $-55.6$  °C for elastomer **E2** (Figure 4b and Table 2).

For the application as a dielectric in DEAs, a high permittivity of the elastomer is highly beneficial as it results in a lower driving voltage of the device. Therefore, elastomers **E2** and **E3B** with a permittivity above 18 have the highest potential for application. The respective monomers can also be synthesized in one day by a condensation reaction, compared to the monomers of elastomers **E4** and **E5**, which have to be synthesized by a hydrosilylation reaction. The hydrosilylation reaction takes several days at  $110$  °C, as the nitrile group interacts with the platinum catalyst. In the end, both elastomers show excellent properties to be applied as self-healing, high-permittivity elastomers in DEAs.

Table 2: Permittivity at  $10^6$  Hz and  $T_g$  of the four elastomers with different cyanoalkyl side groups. Permittivity and  $T_g$  decrease with an increasing number of  $\text{CH}_2$  groups between the silicone backbone and the nitrile groups.

Elastomer	$\epsilon'$ at $10^6$ Hz	$T_g$ [ $^{\circ}\text{C}$ ]
E2	$18.5 \pm 0.2$	-55.6
E3B	$18.1 \pm 0.2$	-59.7
E4	$14.3 \pm 0.4$	-63.6
E5	$11.4 \pm 0.2$	-64.3

#### 4. CONCLUSION

We have demonstrated a synthetic approach to obtain nitrile-functional high-permittivity silicone elastomers in a solvent-free reaction. The mechanical properties can be easily tuned by changing the amount of polar cross-linker. For the optimum concentration of 15 wt% cross-linker, a strain at break of 71% and a modulus of 165 kPa were measured. We synthesized four different elastomers, which varied in the number of  $\text{CH}_2$  groups between the silicone backbone and the nitrile group and characterized their dielectric properties. This allows us to quantify the influence of the alkyl spacer on the glass transition temperature and the relative permittivity of the elastomers. The permittivity decreases with the increasing length of the alkyl spacer from 18.5 for the elastomer with cyanoethyl groups to 11.4 for the elastomer with cyanopentyl groups. This decrease can be explained by the lower concentration of polar nitrile groups in the elastomer, which results in a lower concentration of dipoles. At the same time, the  $T_g$  decreases from  $-55.6^{\circ}\text{C}$  for the elastomer with cyanoethyl groups to  $-64.3^{\circ}\text{C}$  for the elastomer with cyanopentyl groups. The decrease in  $T_g$  results from the increasing polymer chain segment mobility when lowering the dipole concentration. We conclude that the elastomers with cyanoethyl and cyanopropyl groups are most suitable for application in DEAs, due to their high permittivity of more than 18 and the scalable synthesis from nitrile-functional chlorosilanes. Both elastomers have a high potential to find application as self-healable dielectric elastomers in soft actuators and sensors.

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