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Synthesis and characterization of silicones containing cyanopropyl groups and their use in dielectric elastomer actuators

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Abstract

Polydimethylsiloxanes (PDMS) have recently been used as dielectric elastomer materials in electromechanical actuators. When soft enough, electric fields can change their shape. However, due to their low dielectric permittivity, large electric fields are required to induce a change. The approach presented here is to chemically modify silicones with cyanopropyl groups in order to increase their permittivity. Samples containing repeat units with cyanopropyl groups from 3 to 23% were synthesized, whereby different methods were employed. The prepared polymers were cross-linked into thin films. The dielectric permittivity of these films increased from 2.4 (for the silicone matrix) to 6.5 for a film containing about 23% of cyanopropyl repeat units. The most promising materials were further optimized to meet the requirements for actuators and their electromechanic properties were investigated. Material **A** for example, which is a blend of PDMS and cyanopropyl-modified silicone, has a permittivity of 3.5 and higher moduli of elasticity as compared to the matrix and nevertheless shows 10% actuation strain at 40 V/ μm which is a factor of 3.8 larger as compared to the matrix (2.6% actuation strain at the same voltage).

1. Introduction

To exploit the large number of potential applications of dielectric elastomer actuators (DEA), it would be desirable to have specially designed materials at hand with which to optimally address each particular application.[1] DEA are stretchable capacitors that undergo elongation when a voltage is applied to their electrodes.[2] There are quite a few commercial elastomer materials available; they, however, were not designed so as to ideally meet the requirements for DEA.[3] These materials include acrylic foil (VHB),[4] silicones,[5] polyurethanes,[6] and some polystyrene/polybutadiene copolymers[7]. An optimal elastomer for a DEA combines excellent mechanical properties with high permittivity (ϵ) and high breakdown strength. While the above elastomers may have useful mechanical

properties they suffer from an unattractively low permittivity. Consequently, relatively high voltages in the kV regime are needed for operation with all the disadvantages associated with this. Research should therefore concentrate on improving the permittivity as far as possible without sacrificing the elastic properties too much and also having an eye on the breakdown field. For increasing the permittivity of an elastomer, several approaches were used in the literature e.g. blending with high ϵ ceramic particles, phthalocyanines, or conductive fillers as well as by attaching polar groups to the polymer chain.[8]

Silicones attracted the interest of the DEA community during the last few years because they are resistant to oxygen, ozone, and sun-light irradiation and therefore resistant to weathering and ageing.[9] Additionally, they have high shear stability, good dielectric strength, and low toxicity. Besides their good performance at extreme temperatures and the overall small impact of temperature on properties, they are characterized by environmental compatibility during manufacture and use.[10] They suffer, however, of a low permittivity and low fracture resistance that makes the handling of thin films difficult and reduces their electromechanical performance.[11] Prompted by a recent publication on the use of cyano-modified silicones as DEA materials[12] we wish to disclose our findings in this field.[13]

This work utilizes the attractive feature of certain silicones to introduce various polar groups onto the main chain by cleanly proceeding and robust post polymerization modifications. We were able to introduce cyano groups to silicone in varying fractions without negatively affecting the cross-linking capability of the silicones obtained, - a feature that is essential in regard to mechanical properties. Thus, we prepared silicones containing different proportions of polar cyanopropyl groups, cross-linked them in thin films and investigated their dielectric properties as function of the amount of polar groups contained. The most promising materials were further optimized and their mechanical and electromechanical properties were investigated.

2. Results and discussions

Although there is some literature available on the synthesis of polar silicones, including those containing cyanopropyl groups, limited information about their mechanical and electrical properties was provided.[12-14] Additionally, limited information on cross-linking of cyanopropyl functionalized silicones, a key step for DEA applications is available.[15] Their synthesis rests on ring-opening copolymerization of 1,3,5,7-tetra(3-cyanopropyl)-1,3,5,7-tetramethylcyclotetrasiloxane (D_4^{CN}) and octamethylcyclotetrasiloxane (D_4) or polycondensation of either dichloro(3-cyanopropyl)methylsilane or dimethoxy(3-cyanopropyl)methylsilane.[16, 17]

In order to introduce the cyano groups on the silicone, we tried three alternative methods, all of them based on cationic ring-opening polymerization and hydrosilylation reactions in different combinations: a) hydrosilylation of allyl cyanide on a high molecular weight poly(dimethylsiloxane-co-methylhydrosiloxane) ($MH_{(x\%)}$, where x represents the % of Si-H repeat units (r.u.) in polymer), b) redistribution-equilibration reaction of a high molecular weight PDMS with D_4^{CN} , and c) cationic ring opening copolymerization of D_4 and D_4^{CN} . These reactions allowed us to prepare several samples

containing different proportion of cyanopropyl groups named as: $^x\text{CoCN}_{(y\%)}$, where x represents the polymerization method and y the % of cyanopropyl repeat units in the polymer.

2.1. Hydrosilylation of poly(dimethyl-co-methylhydrosiloxane) by allyl cyanide

A poly(dimethyl-co-methylhydrosiloxane)- α,ω -diol ($\text{MH}_{7\%}$) was first prepared by copolymerization of D_4 with 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^{H}) in presence of the cation-exchanger Purolite CT-175 catalyst under equilibrium conditions (Scheme 1a). This step was followed by a hydrosilylation reaction with allyl cyanide in the presence of Karstedt's catalyst. Hydrosilylation allows introduction of various functional groups on silicones,[18-20] but incomplete conversion of the Si-H groups was sometimes reported.

Scheme 1. Synthesis of cyanopropyl modified polysiloxanes: a) hydrosilylation of allyl cyanide on a high molecular weight poly(dimethyl-co-methylhydrosiloxane) obtained by copolymerization of D_4 with D_4^{H} , b) anionic ring opening polymerization of D_4 followed by redistribution-equilibration reaction of a high molecular weight PDMS with D_4^{CN} , and c) cationic ring opening copolymerization of D_4 and D_4^{CN} . These reactions allowed us to prepare several samples containing different proportion of cyanopropyl groups.

Although this method uses a high molecular weight starting copolymer $\text{MH}_{(7\%)}$, ($M_w = 110000$ g/mol), which would ensure good mechanical properties for the final material, an un-controlled self-crosslinking occurred. This side reaction was observed before.[21] In order to understand and avoid it, a model reaction was used. The starting copolymer and either Karstedt's or Speier's catalyst were mixed together. A cross-linking reaction occurred very fast. We believed that the main reason behind this is the presence of $-\text{OH}$ terminal groups, which act as cross-linking sites. When the same catalyst was used as for the hydrosilylation, a dehydrocoupling reaction is possible, involving Si-H and Si-OH groups. By blocking the chain ends, this side reaction can be avoided. Thus, in a second attempt, D_4

and a poly(methylhydrosiloxane) blocked with trimethylsilane end groups were equilibrated in the presence of the cation exchanger and gave a copolymer $\text{MH}_{(13\%)}$ with $M_w = 33000$ g/mol. This copolymer was further used in hydrosilylation and afforded sample $^a\text{CoCN}_{(11\%)}$, (see Figure 2d for ^1H NMR). In this case, the cross-linking attempt using ethyltriacetoxysilane (ETAS) and Ti catalyst was successful, in spite of blocked chain ends. The only reasonable explanation for this behavior is the partial hydrolysis of few unreacted Si-H groups and subsequent inter-chain condensation. Such dehydrocoupling reaction was thoroughly studied by West et al.[22] They reported cross-linked by-products in the alcoholysis of poly(methylhydrosiloxane) with Speier or Karstedt catalysts.[23] The FT-IR spectra of $\text{MH}_{(7\%)}$ and $\text{MH}_{(13\%)}$ are similar (Figure 1) and show the absorption band characteristic for the Si-H bond, at 2157 cm^{-1} , as well as the siloxane bands at $1022\text{--}1093\text{ cm}^{-1}$ (Si-O-Si asymmetric stretch, typical pattern for polymers), 743 and 801 cm^{-1} (γ Si-CH₃), 1261 cm^{-1} (δ Si-CH₃). The bands in the wavenumber range $3700\text{--}3200\text{ cm}^{-1}$ are assigned to silanol SiO-H stretch.[24]

Figure 1. FT-IR spectrum of the starting copolymer $\text{MH}_{(7\%)}$

Due to the mentioned side-reaction, the as obtained 3-cyanopropyl modified copolymers could not be characterized properly by NMR and GPC. Soluble samples were taken before gelation: $^a\text{CoCN}_{(4\%)}$, $^a\text{CoCN}_{(11\%)}$ and their composition was found by ^1H NMR (Figure 2).

2.2. Redistribution-equilibration reaction of PDMS with D_4^{CN}

D_4^{CN} was obtained by hydrosilylation of D_4^{H} with allyl cyanide (Scheme 1). The disappearance of the Si-H band at 2155 cm^{-1} of the starting material in the FT-IR spectrum and the appearance of a new band at 2246 cm^{-1} typical for CN groups, confirmed the reaction. In the ^1H NMR spectrum, the Si-H chemical shift at 4.74 ppm completely disappeared and the set of CH₂ protons from the cyanopropyl siloxane units appeared at 0.75, 1.73, and 2.43 ppm. The starting polydimethylsiloxane- α,ω -diol was prepared by anionic ring-opening polymerization of D_4 in presence of tetramethylammonium hydroxide (TMAH) and tetrahydrofuran (THF) as promoter and solvent (Scheme 1b).[25,26] The molecular weight of the resulted polymer, determined by GPC (in chloroform) was $M_n = 59140$ g/mol, $M_w = 100260$ g/mol, $PDI = 1.7$. The redistribution-equilibration reaction was done using heterogeneous cation exchanger catalysis[27,28] as described in the experimental part. After the redistribution, the molecular weight of the resulting copolymer $^b\text{CoCN}_{(4.3\%)}$ was determined by GPC in THF against polystyrene standards and gave the following values $M_n = 81722$ g/mol, $M_w = 149963$ g/mol, $PDI =$

1.8. Based on ^1H NMR spectrum (Figure 2) the ratio between dimethyl- and (3-cyanopropyl)methylsiloxane units was found to be 22 : 1 (about 4.3% functional groups).

Figure 2. ^1H NMR spectra of the prepared copolymers: a) $^a\text{CoCN}_{(4\%)}$; b) $^b\text{CoCN}_{(4.3\%)}$; c) $^c\text{CoCN}_{(9\%)}$; d) $^a\text{CoCN}_{(11\%)}$; e) $^c\text{CoCN}_{(23\%)}$. The peak at 4.74 ppm in the spectra a) and d) are due to the Si-H protons which did not react in the hydrosilylation.

The great advantage of this method is the possibility to obtain high molecular weight copolymers with various compositions, without side-reactions leading to un-controlled cross-linking. The precursors' ratio and the reaction time are two key elements that govern the final composition of the copolymer. Additionally, mild conditions are required for the last step. In this procedure, only the precursor D_4^{CN} has to be obtained in thorough dry conditions, while the redistribution reaction can be performed with only normal precaution against excessive humidity. The drawback of this method rest in the fact that the unreacted cyclic compounds have to be removed by selective precipitation since the distillation is not effective for cyanopropyl containing cycles.

2.3. Cationic ring opening copolymerization of D_4 and D_4^{CN}

Although D_4^{CN} undergoes anionic polymerization, here we tested the cationic process, by using heterogeneous catalysts. In this case, D_4^{CN} was copolymerized with D_4 in different proportions to yield polysiloxanes with cyanopropyl pendant functional groups in the presence of cation exchangers (Scheme 1c). In addition to the fact that the catalysts are easy to remove by filtration, no neutralization step is required. We used two types of cation exchangers having similar exchange capacity but different characteristics, in different steps of the same reaction. Since D_4^{CN} and D_4 are not miscible, and given the heterogenic nature of the catalytic system that we have chosen, solvents had to be used in order to get a single liquid phase although it is known that the solvents added during polymerization favor the formation of cyclic compounds. In this approach, the catalyst that we usually use for ring

opening polymerization of D_4 , dried Purolite cation exchanger, didn't give the expected results when used alone. On the other hand, we had previously used Amberlite gel cation exchanger (with about 50% water content) for the deprotection of trimethylsilylated OH groups in the case of monosaccharide-modified polysiloxanes[29] and observed that, depending on the substrate's solubility, this catalyst may affect or not the siloxane chain. Using this knowledge and taking into account that D_4^{CN} has hydrophilic groups, we presumed that Amberlite will enhance the chance to open this ring in a cationic process performed in solution. The high water content of the catalyst facilitates the formation of silanol small fragments by breakage of the Si-O-Si linkages. This step is a preliminary one in the cationic polymerization process.

In Figure 3, the GPC curves at different stages of the copolymerization process are shown, i.e. after the preliminary step with Amberlite (a) and after the final step, with Purolite (b). It can be clearly observed that after treatment with Amberlite, only a small amount of relatively high molecular weight species is present, while most of the sample consists of low molecular weight species. Nevertheless, we do not recover the initial cyclics, which shows that the reaction proceeded to a certain level –we consider this reaction mixture as a pre-polymer. Continuing the same reaction with the dry catalyst (Purolite), not only the molecular weight of the polymer increased significantly, but its proportion became the most important.

Figure 3. The GPC curves for the copolymer ${}^cCoCN_{(9\%)}$ prepared by ring opening polymerization of D_4 and D_4^{CN} using two cation exchangers: preliminary step with Amberlite (a) and subsequent polymerization with Purolite (b).

In Figure 4, the FT-IR spectrum of copolymer ${}^cCoCN_{(23\%)}$ is presented. The bands at 2247 cm^{-1} corresponding to the cyano group, at $1018\text{--}1085\text{ cm}^{-1}$ are due to the Si-O-Si asymmetric stretch showing typical shape for polymers, at 743 and 801 cm^{-1} are due to the γ Si-CH₃, and at 1261 cm^{-1} are due to δ Si-CH₃.

Figure 4. FT-IR spectrum of copolymer ^cCoCN_(23%).

From all the above reactions, random copolymers with different content of cyanopropyl groups are formed. This could be benefic, taking into account that the dipoles have to be far enough from each other in order to hinder antiparallel pair formation. While the ¹H NMR spectra of all prepared polymers showed the same peaks (Figure 2), their intensities were different since the proportion of cyanopropyl groups was different. The content of the cyanopropyl groups was calculated from the CH₂ /CH₃ integral ratio.

In the ¹³C NMR spectra of copolymers, the peak for C atoms from the cyano group appear at 119.5 ppm, while those for the propyl groups appear at 20.2, 19.7 and 16.8 ppm and for the CH₃-Si carbons are at 0.97 and -0.59 ppm.

3. Film formation and characterization

Most polysiloxanes are liquids at ambient temperature and to prepare free standing films, the polymer chains have to be cross-linked. The polymers prepared by the three different methods described above produced hydroxy-functionalized polymers. Those hydroxy groups were further used for cross linking which was achieved by a condensation reaction with ethyltriacetoxysilane in the presence of titanium tetra(2-ethylhexoxide) catalyst. Thin films of about 150 μm were made by Blade technique. Gratifyingly, all polymers underwent cross-linking and the dielectric properties of the resulting films could therefore be investigated. Figure 5 shows the permittivity, dielectric loss, and conductivity as function of frequency for films containing different proportions of cyano groups repeat units.

Table 1. The dielectric permittivity at 10⁴ Hz of films containing different % of cyanopropyl repeat units.

Entry	Polymer	r.u.% of CN groups	ε' @ 10 ⁴ Hz
1	PDMS	0%	2.4
2	^a CoCN _(4%)	4%	3.1
3	^b CoCN _(4.3%)	4.3%	3.0
4	^a CoCN _(6%)	6%	3.6
5	^c CoCN _(9%)	9%	4.7
6	^a CoCN _(11%)	11%	5.6
7	^c CoCN _(23%)	23%	6.5

Where $^x\text{CoCN}_{(y\%)}$ where x represents the polymerization method and y the % of cyanopropyl repeat units in the polymer.

Figure 5. Dielectric properties of silicones containing different % of cyanopropyl repeat units.

With an increasing amount of polar groups, the permittivity increased from $\epsilon = 2.4$ for parent PDMS to $\epsilon = 3.0 - 3.6$ for films with 4 - 6 % cyano groups and further to $\epsilon = 6.5$ for 23% cyano groups (Table 1). While at first glance this looked attractive, the conductivity data and also the mechanical properties excluded many of the samples. For example, the conductivity at low frequencies increased from $\sigma = 2.7 \times 10^{-10} \text{ (Ohm} \cdot \text{m)}^{-1}$ for the PDMS matrix to $\sigma = 4 \times 10^{-9} \text{ (Ohm} \cdot \text{m)}^{-1}$ for films containing 4-11% cyano groups. Also, a sudden increase in conductivity was observed for the sample $^c\text{CoCN}_{(23\%)}$ which went up to $\sigma = 3.9 \times 10^{-7} \text{ (Ohm} \cdot \text{m)}^{-1}$. Additionally, the films prepared from $^c\text{CoCN}_{(23\%)}$ had poor mechanical properties, most likely because of the low molecular weight of the prepared polymer and thus high crosslinking density that leads to a more brittle film. Samples $^a\text{CoCN}_{(4\%)}$ and $^a\text{CoCN}_{(6\%)}$ were excluded because their synthesis did not allow for a good control of cross linking. Polymer $^a\text{CoCN}_{(11\%)}$ obtained by hydrosilylation had attractive permittivity and low conductivity. Additionally, its synthesis allowed large scale preparation of copolymers with high molecular weight. However, thin films of it did not have excellent mechanical properties. To improve on this, $^a\text{CoCN}_{(11\%)}$ was blended in PDMS matrix in different weight percentages: 50, 40, 33, 28 and 16. All samples were investigated for their mechanical properties and permittivity (not shown). The sample with 28% of $^a\text{CoCN}_{(11\%)}$ in PDMS was found to be optimal, resulting in “material A” that shows both excellent mechanical properties (Figure 6) and an increased permittivity ($\epsilon = 3.5$). This material was made even softer by reducing the amount of cross linker (material B). The stress strain curves for **A** and **B** as well as for pure crosslinked PDMS matrix

are given in Figure 6. Table 2 summarizes the elastic moduli at different strain levels, F_{max} , and the strain at break.

Table 2. The permittivity at high frequencies, the elastic moduli (Y) at different strain levels and the strain at break. At least three samples were measured and the results were averaged.

Entry	ϵ	Y [kPa] 1% strain	Y [kPa] 10% strain	Y [kPa] 20% strain	Y [kPa] 50% strain	Y [kPa] 100% strain	F_{max} N/mm ²	Strain at break [%]
A	3.5	1593	712	617	460	354	0.78	228
B	3.5	1056	363	307	225	172	0.59	302
^b CoCN _(4.3%)	3.0	4367	639	499	348	258	1.19	443
PDMS	2.4	3187	774.5	582	416	301	0.93	416

As discussed above, most of the cross linked materials (Table 1) had unsatisfactory mechanical properties, however, there was still one sample, ^bCoCN_(4.3%), where the electrical and mechanical properties met the requirements for DEA. Films had good elastic properties with a strain at break of 443% as illustrated in Figure 6. Its moduli of elasticity at different strains are given in Table 2.

Figure 6. Stress strain curves of the improved materials ^bCoCN_(4.3%), **A** and **B** as well as the PDMS matrix. The curves are the average of at least three samples.

Materials ^bCoCN_(4.3%), **A**, **B**, and PDMS matrix were investigated electromechanically as described in the experimental part. The lateral actuation strains are shown in Figure 7 as a function of the electric field. The actuation strains at 20 V/ μ m for PDMS and ^bCoCN_(4.3%), as well as the composites **A** and **B** were 0.65%, 1.2%, 1.4% and 6%. The actuation at breakdown for composite **B** was 8% at 22 V/ μ m, for composite **A** was 11.8% at 42 V/ μ m, while for ^bCoCN_(4.3%) a lateral actuation strain of 6.2% at 37.5 V/ μ m was measured. Since **A** and **B** have the same value for the permittivity, the improvement in the actuation strain of **B** is mainly due to its lower elastic moduli as compared to **A**. Despite of the fact that **A** had higher moduli of elasticity at strains higher than 20% as compared to the

matrix, it nevertheless shows 10% actuation strain at 40 V/ μm which is much larger as compared to the matrix (2.6% at the same voltage).

Figure 7. Lateral actuation strain of membrane actuators for PDMS matrix, **A** and **B** as a function of applied voltage. The actuator made of ${}^b\text{CoCN}_{(4.3\%)}$ was prestrained by hand ($\sim 10\%$). For all other actuators a 30% prestrain was used.

The performance of composites **A** and **B** as well as of the matrix was further investigated for their long-term stability under high voltages and was found that they were stable and survived thousands of cycles. Figure 8 displays the actuation strain versus time for an actuator made of **A** activated by a sinusoidal voltage with a peak value of 3000 V (31 V/ μm) at 2.5 Hz. Some viscoelastic losses are observed for both materials, which, if needed, could easily be compensated by running several cycles before the “real” actuation.

Figure 8. Long-term stability of **A** at 2.5 Hz and 3000 V (31 V/ μm). Some hysteresis was observed but only in the first cycles.

In order to verify the physical origin of the losses (mechanical or electrical) further mechanical investigations were done. Figure 9 shows mechanical relaxation tests on **A**, **B** and matrix. The samples were prestrained by 35% and relaxed to 30% strain so as to mimic 5% actuation strain in an electromechanical test. The materials were tested for 100 cycles at a speed of 10 mm/s. As can be seen, samples **A** and **B** show quite large viscoelastic losses at the beginning of the cycles. After about 15 cycles, however, no further relaxation was observed in both materials. Further investigations are on the way to reduce the losses by blending.

Figure 9. Stress versus time for PDMS and samples **A** and **B** prestrained 35% and relaxed to 30% for 100 cycles at a speed of 10 mm/s.

4. Experimental part

Materials

Octamethylcyclotetrasiloxane >98%, 1,3,5,7-tetramethylcyclotetrasiloxane, allyl cyanide, 98%, tetramethylammonium hydroxide (TMAH) solution 25 wt% in water from Fluka. Linear hydroxyl end functionalized silicone (PDMS) ($M_w=139,000$ g/mol), ethyltriacetoxysilane (ETAS) by ABCR, titanium 2-ethylhexoxide from Aldrich. Purolite CT-175 - a macroporous styrene-divinylbenzene copolymer with sulfonic groups, supplied by Viomet S.A (volume exchange capacity, 1.8 meq/ml; gravimetric exchange capacity, 4.9 meq/g; specific surface, 35 m²/g). Amberlite IR-120(plus), a strongly acidic gel-type resin with sulfonic acid functionality, having total exchange capacity of 1.9 meq/ml, was supplied by Aldrich and used as received. Poly(methylhydrosiloxane), trimethylsilyl terminated L-31 ($M_w = 2560$ g/mol), having a viscosity of 18 cSt (25°C) was supplied by Union Carbide.

Characterization methods

The infrared spectra were registered on a Bruker Vertex 70 FT-IR instrument, in transmission mode, in the 300-4000 cm^{-1} range (resolution 2 cm^{-1} , 32 scans), at ambient temperature. ^1H NMR spectra were registered on 400 MHz Bruker spectrometer in CDCl_3 without internal standard. GPC measurements were made in chloroform or THF on a PL-EMD 950 Chromatograph - Evaporative Mass Detector. The calibration was performed with polystyrene standards.

The equipment and experimental procedures for dielectric measurements, mechanical properties, and actuator test have been described previously.[30] Actuator tests were performed using circular membrane actuators, for which the silicone films were prestrained (30 %) and thereafter fixed between two circular frames (2 cm diameter). Circular electrodes (8 mm diameter) of carbon black powder were applied to each side of the film.

Synthesis of the precursors

Synthesis of $\text{MH}_{(7\%)}$

D_4 (19 ml, 18.16 g, 61.2 mmol), D_4^{H} (1 ml, 0.98 g, 4.1 mmol), and Purolite CT-175 catalyst (0.5 g) were introduced in a two-necked flask equipped with a reflux condenser and mechanical stirrer. The mixture was stirred for 2h at 80 $^{\circ}\text{C}$ and then the catalyst was filtrated. The reaction mixture was devolatilized by heating at 150 $^{\circ}\text{C}/5$ mmHg. The composition and molecular mass of the resulted copolymer were evaluated by ^1H NMR, and GPC, respectively. $M_n = 82300$ g/mol, $M_w = 110400$ g/mol, $PDI = 1.3$. The content in Si-H groups (7 %) was estimated on the basis of ^1H NMR spectrum by comparing the intensity of the Si-H signal with that of the Si- CH_3 . ^1H NMR (CDCl_3): $\delta = 4.68$ (Si-H, 1H); 0.14 -0.07 (Si(H)- CH_3 , and Si(CH_3) $_2$, 86H).

Synthesis of $\text{MH}_{(13\%)}$

D_4 (83.2 ml, 79.54 g, 0.27 mol), poly(methylhydrosiloxane), L-31 (16.8 ml), and Purolite CT-175 catalyst (2.5 g) were introduced in a two-necked flask equipped with reflux condenser and mechanical stirrer. The mixture was stirred for 3 h at 90-100 $^{\circ}\text{C}$. Then the catalyst was removed by filtration. The reaction mixture was devolatilized by heating at 150 $^{\circ}\text{C}/5$ mmHg (6.5 ml cyclic compounds were removed). The molecular mass of the resulted copolymer was evaluated by GPC: $M_n = 16254$ g/mol, $M_w = 33027$ g/mol, $PDI = 2.03$. The content in Si-H group estimated on the basis of ^1H NMR spectrum was 13% mol. ^1H NMR (CDCl_3): $\delta = 4.70$ (Si-H, 1H); 0.20 - 0.05 (Si(H)- CH_3 , and Si(CH_3) $_2$, 43H).

Synthesis of polydimethylsiloxane- α,ω -diol (PDMS)

A 25% solution of TMAH in water (1 μl) and benzene (5 ml) was introduced in a three-necked flask equipped with a Dean–Stark trap and a reflux condenser with CaCl_2 protection. After the water was distilled off by azeotropic distillation, the solvent was completely removed by vacuum distillation leaving the dried white solid of TMAH in the flask. To this, dried THF (10 ml) and D_4 (10 ml, 9.56 g, 32.2 mmol) were added and the mixture was stirred at 80 $^{\circ}\text{C}$ for 3.5 h. Then the temperature was increased to 150 $^{\circ}\text{C}$ for 1 h to remove THF and decompose the catalyst. Finally, the polymer was vacuumed at room temperature for degassing and then at 150 $^{\circ}\text{C}$ to remove the eventually equilibrium cycles. Molecular mass estimated by GPC: $M_n = 59140$ g/mol, $M_w = 100260$ g/mol, $PDI = 1.7$. ^1H NMR (CDCl_3): $\delta = 0.072$ (Si(CH_3) $_2$).

Synthesis of $^a\text{CoCN}_{(4\%)}$

Copolymer MH_(7%) (1.9 g) was dissolved in dried toluene (40 ml). Then, allyl cyanide (0.18 ml, 0.15 g, 2.23 mmol, 30 % excess) and Karstedt catalyst (30 μ l) were added and the reaction was carried on under argon, for 10 h at 70 °C. A thick solution (gel) formed, to which the cross-linking agents were subsequently added.

¹H NMR (CDCl₃) δ : 4.72 (unreacted Si-H, s, 0.58 H), 2.39 (NC-CH₂-CH₂-CH₂, 2H), 1.77 (NC-CH₂-CH₂-CH₂, 2H), 0.71 (NC-CH₂-CH₂-CH₂-Si, 2H), 0.19-0.11(Si-CH₃, 146H).

Synthesis of ^aCoCN_(6%)

Was obtained similarly as ^aCoCN_(4%), but the reaction conditions were modified as follows: a larger excess of allyl cyanide was used (a total of 300%), added in three steps, and the reaction proceeded for 25 h at 60 °C.

¹H NMR (CDCl₃) δ : 4.72 (Si-H, 0.35H), 2.40 (NC-CH₂-CH₂-CH₂, 2H), 1.77 (NC-CH₂-CH₂-CH₂, 2H), 0.72 (NC-CH₂-CH₂-CH₂-Si, 2H), 0.18-0.11(Si-CH₃, 103H).

Synthesis of ^aCoCN_(11%)

The procedure was similar to that for ^aCoCN_(4%), with the following exceptions: the starting substrate copolymer was MH_(13%), the excess of allyl cyanide was 50% and the reaction was let for 25 h at 75°C.

¹H NMR (CDCl₃) δ : 4.72 (Si-H, 0.28H), 2.39 (NC-CH₂-CH₂-CH₂, 2H), 1.76 (NC-CH₂-CH₂-CH₂, 2H), 0.73 (NC-CH₂-CH₂-CH₂-Si, 2H), 0.18-0.09(Si-CH₃, 53H).

Synthesis of ^bCoCN_(4.3%)

The high molecular weight polydimethylsiloxane- α,ω -diol (0.8 g, 10.8 mmole dimethylsiloxane units) and D₄^{CN} (0.1 g, 0.79 mmole cyanopropylsiloxane units) were mixed in THF (10 ml). Then, cation exchanger (Purolite CT-175) (0.02 g) was added and the mixture was heated to reflux for 15 h. The catalyst was filtered off, and the solvent was removed under vacuum. The crude product was washed thrice with methanol. GPC in THF: M_n = 81700 g/mol, M_w = 150000, PDI = 1.8; ¹H NMR (CDCl₃) δ : 2.44 (NC-CH₂-CH₂-CH₂, 2H), 1.76 (NC-CH₂-CH₂-CH₂, 2H), 0.77 (NC-CH₂-CH₂-CH₂-Si, 2H), 0.19-0.05 (Si-CH₃, 137H).

Synthesis of ^cCoCN_(9%)

D₄^{CN} (0.65 g, 1.28 mmol) and D₄ (3.03 g, 10.24 mmol) were dissolved in THF:methanol = 1:1 vol (6 ml). Then Amberlite cation exchanger in gel form (0.3 g) was added and the reaction temperature was raised to 70°C. After 12 h, the catalyst was filtered off and the solvents were removed under reduced pressure. The as-obtained pre-polymer was mixed with dried Purolite cation exchanger (0.1 g) and the reaction was continued in bulk at 80 °C for 15 h. The catalyst was filtered off and the solvent was removed. GPC in THF: M_n = 30131 g/mol, M_w = 67920, PDI = 2.25; ¹H NMR (CDCl₃) δ : 2.42 (NC-CH₂-CH₂-CH₂, 2H), 1.75 (NC-CH₂-CH₂-CH₂, 2H), 0.75 (NC-CH₂-CH₂-CH₂-Si, 2H), 0.23-0.11 (Si-CH₃, 64H); ¹H NMR calculations gave a content of 9% functional groups. ¹³C NMR (CDCl₃) δ : 119.5, 20.3, 19.7, 16.8, 0.97, -0.59.

Synthesis of ^cCoCN_(23%)

In a similar way, the copolymer ^cCoCN_(23%) was obtained with 23% CN-propyl groups. GPC in THF: M_n = 20652 g/mol, M_w = 39873 g/mol, PDI = 1.9; ¹H NMR (CDCl₃) δ : 2.41 (NC-CH₂-CH₂-CH₂, 2H), 1.75 (NC-CH₂-CH₂-CH₂, 2H), 0.72 (NC-CH₂-CH₂-CH₂-Si, 2H), 0.18-0.11 (Si-CH₃, 22H).

Cross linking of the polymers with different content of cyanopropyl groups in thin films

All the prepared polymers were cross linked by using the same amount of cross linker. E.g. to 0.5 g polar silicone, ETAS (0.1 g) was added. The viscosity of the mixture was adjusted with toluene to allow us having the desired viscosity for thin film formation. Then the titanium 2-ethylhexoxide (10 μ l, 50% solution in toluene) was added and the films were made by using doctor Blade technique. The quality of the prepared films was sufficiently good for all the films to do the dielectric measurements, but unfortunately not sufficiently good for the mechanical and electromechanical tests. They are described as: ^aCoCN_(4%) very good mechanical properties, ^aCoCN_(6%) very good mechanical properties, ^aCoCN_(11%) good mechanical properties, ^bCoCN_(4.3%) good mechanical properties, ^cCoCN_(9%) ruptured easily, ^cCoCN_(23%) is brittle.

Blends of ^aCoCN_(11%) in PDMS

To a 20 wt % solution of silicone ^aCoCN_(11%) in toluene (5 ml), 2.5 g of a Si-OH end functionalized polydimethylsiloxane ($M_w = 139000$ g/mol) and different amounts of cross linker ETAS were added and mixed to form a homogenous solution (See Table 3). To this mixture, titanium 2-ethylhexoxide solution in toluene (50 wt%) (150 μ l) was added and the film was made immediately by doctor Blade technique.

Table 3.

PDMS: ^a CoCN _(11%)	Sol 20% ^a CoCN _(11%) (ml)	PDMS-OH (g)	ETAS* (ml)	Ti cat 50% (μ l)
A	5	2.5	0.5	150
B	5	2.5	0.4	150

*By further reducing the amount of cross-linker to 0.3 ml resulted in slightly cross linked films or to 0.2 ml the film did not cross linked.

5. Conclusion

Three different synthetic paths were evaluated for the synthesis of silicone with cyanopropyl pendant groups namely: a) hydrosilylation of allyl cyanide on a high molecular weight poly(dimethyl-co-methylhydrosiloxane), b) redistribution-equilibration reaction of a high molecular weight PDMS with D₄^{CN}, and c) cationic ring opening copolymerization of octamethylcyclotetrasiloxane (D₄) and D₄^{CN}. These reactions allowed us to prepare several samples containing different proportion of cyanopropyl groups. Additionally, the prepared polymers are functionalized with hydroxyl end groups which were used for the cross linking in thin films. All the prepared polymers allowed thin film formation in the sub 150 μ m range. It was shown that the permittivity of such polymers can be increased with increasing the % of cyanopropyl repeat units from 2.4 for the PDMS matrix to 6.5 for a polymer containing 23 % cyanopropyl groups. Unfortunately, with increasing the amount of cyanopropyl groups the materials are becoming brittle. The most promising approaches for the synthesis were a) and b) since they allowed synthesis of polymers with high molecular weight and also incorporation of cyanopropyl groups in different proportions. The last approach led to polymers that have low molecular weight and therefore their films show poor mechanical properties when cross-linked. The as prepared ^bCoCN_(4.3%) was cross linked to a film that had $\epsilon=3$, excellent mechanical properties, and 6.2% maximum actuation strain at 37.5 V/ μ m. Polymer ^aCoCN_(11%) when blended into PDMS to 28 wt% and cross linked with different amounts of cross linker, allowed formation of good materials (**A** and **B**) with tunable

mechanical properties and $\epsilon=3.5$. The maximum actuation at breakdown for **B** was 8% at 22 V/ μm . Despite that material **A** has higher moduli of elasticity as compared to the matrix, it nevertheless shows 10% actuation strain at 40 V/ μm which is a factor of 3.8 larger as compared to the matrix (2.6% actuation strain at the same voltage). The reason behind this improvement is the increase in the dielectric permittivity. Additionally, such materials are robust and survived many cycles under high electric fields.

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