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Published in:
Bioinspiration & Biomimetics

Link to article, DOI:
[10.1088/1748-3190/abdd9f](https://doi.org/10.1088/1748-3190/abdd9f)

Publication date:
2021

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Tran, J.-A., Madsen, J., & Skov, A. L. (2021). Novel polyrotaxane cross-linkers as a versatile platform for slide-ring silicone. *Bioinspiration & Biomimetics*, 16, [025002]. <https://doi.org/10.1088/1748-3190/abdd9f>

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To cite this article before publication: Jakob-Anhtu Tran *et al* 2021 *Bioinspir. Biomim.* in press <https://doi.org/10.1088/1748-3190/abdd9f>

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Novel polyrotaxane cross-linkers as a versatile platform for slide-ring silicone

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Received xxxxxx
Accepted for publication xxxxxx
Published xxxxxx

Abstract

Slide-ring elastomers have garnered a lot of interest for their potential use in dielectric elastomer actuators due to their intrinsically soft nature and high elasticity. However, the use of sliding cross-linkers has been constrained by their low miscibility with commonly used elastomer precursors and the specialized curing chemistries that are necessary for incorporating them into networks. Here, we have presented a method to produce vinyl functional polyrotaxane cross-linkers that are compatible with polysiloxanes and can be processed by industrially scalable methods. The sliding silicone films that were fabricated with these novel cross-linkers were highly extensible (>350%) and did not exhibit strain hardening even at high elongation. The composite films also retained the favorable dielectric properties of silicone elastomers such as the characteristic low dielectric loss. The modified polyrotaxanes present a robust platform for producing a new class of sliding silicone elastomers with well-defined networks structures.

Keywords: Silicone, slide-ring elastomer, polyrotaxane, dielectric elastomer actuator, DEA

1. Introduction

Dielectric elastomer actuators (DEAs) present a lot of promise in advancing the field of soft robotics and biomimetic design due to their soft and flexible nature, high deformability and lightness in weight [1–3]. Given these inherent characteristics, DEAs offer the potential to emulate the energy transducing characteristics of natural muscles and opening the door to novel technologies that cannot be realized with traditional motors such as self-cleaning surface coatings and tunable elastomeric lenses [4,5]. While commercially available elastomers have been considered as suitable candidate materials for DEAs, there has been a lot of progress in tailoring elastomers specifically for actuation, namely softer materials and/or materials with higher dielectric permittivity. The approaches range from creating composite systems to completely novel chemical compositions [6–8] and network structures [9,10].

Figure 1: The pulley-like behavior of sliding networks

In contrast to conventional elastomers, slide-ring materials demonstrate a novel type of dynamic network structure consisting of mobile cross-links that can rearrange on a molecular scale. The sliding links are formed by ring molecules that have been threaded on linear axis polymers.

This type of supramolecular assembly allows the rings to act as cross-links that can slide on the constrained axis (as seen in Figure 1), thus imparting the networks with an additional degree of entropic freedom [11]. These sliding elastomers have been proven peculiar in their intrinsic softness while maintaining high deformability and toughness [12]. This reversible and soft nature of slide-ring materials makes them ideal candidates for dielectric elastomer actuators provided that they can be designed to be electrically robust too.

Polyethylene glycol (PEG) and α -cyclodextrin (α -CD) based polyrotaxanes have shown promise as a versatile platform for slide-ring materials due to their commercially available components and relative ease of production. While the production of PEG/ α -CD polyrotaxanes has reached a commercial scale, their inclusion in silicone networks has been limited [13,14]. The slide-ring materials that have been utilized for DEA fabrication have so far been restricted to poly- ϵ -caprolactone grafted systems, which have a relatively high elastic modulus (~ 1 MPa) compared to silicone elastomers [15–17]. The use of polysiloxanes or other network chemistries with polyrotaxane cross-linkers is generally restricted by the low reactivity of the pure polyrotaxanes as well as immiscibility issues [18]. Both issues are caused by the dense hydrogen bonding that occurs between the hydroxyl groups of the threaded rings and can be solved by chemical modification of the polyrotaxanes.

Here, we present a synthetic pathway to produce vinyl functional slide-ring cross-linkers that can be processed with common solvents and incorporated into polysiloxane networks through hydrosilylation. This type of curing chemistry is ubiquitous in silicone elastomers due to its high efficiency and selectivity as well as ease to work with [19]. These features are important in ensuring the versatility and scalability of the slide-ring cross-linkers as the basis of a new class of sliding silicone elastomers.

The slide-ring silicone elastomers that were produced with the novel cross-linkers exhibited high softness while maintaining the favorable dielectric properties that are characteristic for silicones. Additionally, the sliding elastomers possessed a highly time dependent relaxation mode resulting from the sliding of links within the polyrotaxane that is not present in traditional silicone networks. This phenomenon demonstrates the possibility of designing more intricate dielectric elastomer transducers with two distinctive modes of behavior determined by the operational speed of the system.

2. Experimental

2.1 Materials

Polyethylene glycol (PEG 35000) was purchased from Fluka. (benzotriazol-1-yloxy)tripyrrolidinophosphonium

hexafluorophosphate (PyBOP) was purchased from Tokyo Chemical Industry Co., Ltd. 1,3-divinyl-1,1,3,3-tetramethyldisilazane, platinum-divinyldimethylsiloxane complex (3.0% Pt) as well as hydride and vinyl terminated polydimethylsiloxanes (PDMS $M_n = 20\,000$ to $24\,000$ g mol⁻¹) were procured from Gelest Inc. Household bleach (Klorin Original, 5% available chlorine) was purchased from a local supplier (Salling group A/S). Sylgard[®]184 elastomer kit was purchased from Dow Chemical Company Ltd. and Ecoflex[™] 00-30 elastomer kit was purchased from FormX Amsterdam. All other chemicals were purchased from Merck KGaA and used as received unless otherwise stated.

2.2 Characterization

¹H-NMR spectra were acquired on a Bruker 300 MHz spectrometer in either deuterated dimethyl sulfoxide (DMSO) or chloroform at ambient temperature unless stated otherwise, with the residual solvent peaks used as the internal standard. Size Exclusion Chromatography (SEC) measurements were conducted with Shimadzu instrumentation (SIL-10AD autoinjector, LC-10AD liquid chromatograph, RID-10A refractive index detector) with a 10 mM LiBr DMSO eluent flow of 1.000 mL/min at room temperature through a Millipore/Waters Ultrastaygel 10⁵ Å column.

Electrical breakdown tests were performed on an in-house built device based on international standards (IEC 60,243–1 (1998) and IEC 60,243–2 (2001)) [20]. A stepwise increase of voltage was applied to the samples (50 V step s⁻¹) at a rate of 0.5 steps s⁻¹. Film thickness was determined through optical microscopy of the film cross-section.

Dielectric relaxation spectroscopy (DRS) was performed at room temperature and low electrical field (~ 1 V mm⁻¹) on a Novocontrol Alpha-A high-performance frequency analyser (Concept 40 Top Class System, Novocontrol Technologies GmbH & Co, Germany) operating in the frequency range 10⁻¹–10⁶ Hz. The samples were approximately 0.1 mm thick and 20 mm in diameter.

Differential scanning calorimetry (DSC Q1000; TA Instruments) measurements were performed on the elastomer samples from -90 to 200 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

Linear viscoelastic analysis (LVE) was conducted on a TA Discovery HR-1 rheometer with 20 mm diameter parallel-plate geometry. The measurements were carried out at a fixed strain amplitude of 1 % with a frequency range of 0.01 to 100 Hz.

The tensile properties of the elastomers were measured using the Instron 3340 materials testing system (INSTRON, US). Samples of 30 mm length and 3.18 mm width were placed between two clamps with an initial separation distance of 20 mm. Strain was defined as $(L - L_0)/L_0$ where L is the distance between the clamps during stretching and L_0 the initial

1 separation distance. The test specimens were elongated
2 uniaxially at a strain rate range of 0.5 to 200 mm min⁻¹.

3 Actuation measurements were performed by connecting the
4 thin film samples (thickness of 110 to 150 μm) with a high
5 voltage power supply (PS375, Stanford Research Systems
6 Inc.) and applying step-wise increased voltages (500 V per
7 step) until electrical breakdown. The samples were mounted
8 with 20% pre-strain on a round plastic frame with an inner
9 diameter of 30 mm. Circular electrodes with a diameter of 10
10 mm were painted on either sides of the samples with carbon
11 grease. The actuation was determined by video analysis
12 software (Tracker).

13 2.3 Preparation of polyrotaxanes

14 To prepare the carboxylic acid terminated PEG-COOH,
15 10 g (0.29 mmol) of PEG was oxidized in 100 mL of DI water
16 with 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO,
17 100 mg, 0.64 mmol), KBr (116 mg, 0.97 mmol) and an
18 aqueous NaClO solution (20 mL, 5% available chlorine) at a
19 pH of 11-12 for 15 min. The oxidation was quenched with
20 10 mL of ethanol. The reaction mixture was then acidified
21 with HCl to a pH below 2. Proper ventilation was ensured by
22 performing the procedure in a fume-hood with a lowered sash
23 to avoid exposure to highly toxic chlorine gas. The product
24 was extracted with two 100 mL aliquots of dichloromethane
25 (DCM) that were then combined and evaporated *in vacuo*. The
26 product was dissolved in 200 mL of hot (60 °C) ethanol and
27 precipitated at -20 °C. The precipitate was then washed with
28 ethanol and dried *in vacuo* overnight. The end-group
29 conversion was confirmed with ¹H-NMR to be >98%.

30 The polyrotaxanes were prepared as follows: 3 g
31 (0.09 mmol, 0.18 mmol carboxylic acid) of PEG-COOH and
32 13.7 g (12.3 mmol) of α-cyclodextrin (α-CD) were dissolved
33 in 100 mL of DI water and stirred for 15 minutes at room
34 temperature before overnight complexation at 5 °C. The
35 complexed pseudo-polyrotaxane (PPR) was then freeze-dried
36 and crushed into a fine powder. The PPR was then end-capped
37 with the addition of 1-adamantylamine (169 mg, 1.1 mmol),
38 PyBOP (581 mg, 1.1 mmol) and N, N-diisopropylethylamine
39 (0.2 mL, 1.2 mmol). The mixture was dissolved in 100 mL of
40 dry N, N-dimethylformamide (DMF) and stirred overnight at
41 RT in an inert atmosphere. The reaction mixture was then
42 washed through centrifugation, twice with a 1 to 1 mixture of
43 DMF/methanol and twice with methanol. The obtained solid
44 was then dissolved in dimethylsulfoxide and precipitated in
45 water, followed by repeated washings with water and freeze-
46 drying.

53 2.4 Preparation of vinyl functional polyrotaxanes (ViPR)

54 The polyrotaxane (1 g, 7.35 μmol) was dissolved in dry
55 DMSO (40 mL) in a nitrogen atmosphere. A premade mixture
56 (4.4 g, 20.4 mmol) of 1,3-divinyl-1,1,3,3,3-

tetramethyldisilazane (DVTMDS) and 1,1,1,3,3,3-
hexamethylsilazane (HMDS) was slowly added to the reaction
vessel in a drop-wise manner. The molar ratio of the silylating
agents was varied between experiments. The reaction mixture
was stirred for 6 hours at 60 °C, followed by addition of dry
toluene (40 mL). The mixture was then left to react for an
additional 20 hours. The product was then precipitated in
methanol (800 mL), washed with methanol and dried under
vacuum, resulting in a white solid (1.2 g, 69% yield).

2.5 Preparation of slide-ring silicone films

Hydride terminated PDMS (0.41 g, $M_n = 24\,000\text{ g mol}^{-1}$),
vinyl terminated PDMS extenders (0.17 g, $M_n = 20\,000\text{ g mol}^{-1}$) and ViPR cross-linkers (0.06 g, $f_{\text{vinyl}} = 0.42\text{ mmol g}^{-1}$) were dissolved in toluene. Platinum catalyst was added (1.1 mg, 50 ppm) and the mixture was left to pre-cure for 10 minutes at 80 °C. The mixture was then cast into a Teflon mold and left to evaporate for a day at room temperature before the final overnight curing at 80 °C. Pure PDMS control films were prepared with identical hydride terminated PDMS (1.4 g, $M_n = 24\,000\text{ g mol}^{-1}$) and vinyl terminated PDMS extenders (0.57 g, $M_n = 20\,000\text{ g mol}^{-1}$) and vinyl functional polysiloxane cross-linkers (0.14 g, $f_{\text{vinyl}} = 0.61\text{ mmol g}^{-1}$). The formulation was mixed on a FlackTek Inc. DAC 150.1 FVZ-K SpeedMixer™ and then coated on a glass substrate using a film applicator (3540 bird, Elcometer, Germany) with a 200 μm blade. Commercial Sylgard®184 and EcoFlex™ 00-30 silicone films were prepared according to the instructions provided by the suppliers.

3. Results and discussion

3.1 Vinyl functional slide-ring cross-linkers

Polyrotaxanes consisting of polyethylene glycol (PEG) and α-cyclodextrin (α-CD) were synthesized according to methods previously described in the literature [21], with minor modifications. An alternative coupling reagent was adopted instead of the commonly used benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate to avoid the formation of the carcinogenic byproduct hexamethylphosphoramide. Additionally, the end-capping reaction was performed at room temperature to inhibit esterification side-reactions that can form polyrotaxane dimers.[21] Size exclusion chromatography was employed to confirm that the threaded α-CDs were trapped by the bulky capping groups at the end of the PEG chains, thus forming a stable supramolecular compound that does not disassociate when dissolved in DMSO. This can be seen in the decreased retention volume of the polyrotaxanes caused by the larger hydrodynamic size compared to the PEG and α-CD precursors (Figure 2). The achieved polyrotaxane yield varied between

Figure 3: Approximate size of a polyrotaxane compound with 100 α -CD rings that have been threaded on a PEG chain with a molecular weight of 35 000 g mol⁻¹. This relates to an inclusion ratio of 25% compared to the theoretical maximum of 400 rings.

60 to 70% based on PEG (α -CD was used in excess). The average number of threaded rings per each PEG chain and the molecular weight of the polyrotaxanes were then determined by ¹H-NMR. The values were attained by integrating the spectral peaks assigned to the adamantane end-groups (labeled a, b and c in Figure 2) of the capped PEG chains and the H1 peak (4.80 ppm) of the cyclodextrin glucose units (see Figure 2).

The degree of ring threading has an inverse relation to the length of the PEG chain [22]. It is thus possible to control the amount of threaded rings based on the molecular weight of the selected chain polymer. In this case, approximately 100 rings were threaded for each polyrotaxane molecule, which corresponds to a threading ratio of 25% compared to the maximum amount of rings that could be fit on the axis chains (as seen in Figure 3). The theoretical maximum is established based on the assumption that one ring fits two ethylene glycol units [23].

The spontaneous threading process is driven by the formation of hydrogen bonds between the cyclodextrin rings when they are aligned by the axis polymers [24]. The threaded complexes are further stabilized by arranging ordered hexagonal packing structures with neighboring compounds

(illustrated in Figure 4) [25,26]. However, the abundant hydrogen bonding between the threaded cyclodextrin rings has been found to both limit the solubility of the final polyrotaxanes and lower the reactivity of threaded rings [18,27]. Additionally, the tendency for the rings to aggregate constricts the sliding phenomena by locking the rings in place [28]. Chemical modification of the threaded α -CD rings was thus necessary to improve the solubility of the compounds in organic solvents and to disrupt the dense intermolecular packing structure. It was also possible to introduce reactive functional groups that are necessary for network formation on the threaded rings during this process. The hydroxyl groups on the threaded α -CD rings were substituted with different molar ratios of commercially available silylating agents HMDS and DVTMDS. The modified polyrotaxanes were prepared by slowly adding a premade mixture of the silylating agents into a rigorously stirred polyrotaxane solution in DMSO. After the initial reaction had progressed for 6 hours, toluene was added to the reaction mixture to increase the degree of modification by preventing the precipitation of the partly silylated polyrotaxanes. The conversion of the hydroxyl groups was confirmed by ¹H-NMR (Table 1).

Figure 2: ¹H-NMR spectrum (300 MHz, d₆-DMSO, 80 °C) and SEC analysis (detector: RI, eluent: 10 mM LiBr in DMSO) of polyrotaxanes.

Figure 4: Packing structure of the threaded cyclodextrin rings

It was possible to control the number of reactive vinyl groups introduced per ring by regulating the feed ratio of the two agents (Figure 5 A and B). Ideally, there should be only one reactive functional group taking part in the network per ring to avoid the formation of fixed junctures on the individual rings (Figure 5C). This well-defined network structure is important to maximize the sliding possibility of the elastomers and to ensure that all of the cross-links are freely mobile in relation to each other. The ability to adjust the number of network participating points on each of the threaded rings offers a higher degree of control than the more commonly used method of grafting side-chains on the numerous hydroxyl groups (18 per ring) of the cyclodextrin rings [12,18,29,30].

Altering the stoichiometric balance of the two silylating agents in the reaction feed was found to effectively control the number of vinyl functional groups per ring and to ensure that the degree of substitution of the hydroxyl groups was sufficient to increase the solubility of the modified polyrotaxane (Table 1). The final polyrotaxane cross-linkers were soluble in industrially common solvents such as

chloroform, toluene, and tetrahydrofuran. The aforementioned solvents can be easily removed during processing thus making it possible to handle the modified polyrotaxanes by industrially scalable methods such as solvent casting. The introduction of vinyl groups allows the cross-linkers to be utilized in silicone networks by means of hydrosilylation curing chemistry, which is widely used in commercial silicone formulations due to its high efficiency and selectivity [19].

Table 1: Effect of the feed ratio of the vinyl functional DVTMDS silylating agent on the final functional group composition of the modified polyrotaxanes (ViPR), where TMS is the unreactive trimethylsilyl group and OH the residual hydroxyl groups. The degree of substitution is determined by the number of hydroxyl groups that were substituted per each glucose unit in the ring.

Feed	Groups per α -CD ring			Degree of substitution
	Vinyl	TMS	OH	
0	0	12.9	5.1	2.15
0.25	0.6	12.0	5.3	2.11
0.35	1.0	10.5	6.6	1.91
0.51	2.1	11.2	4.7	2.21
0.73	5.3	8.1	4.6	2.24
1	11.0	0	7.0	1.83

3.2 Formulating slide-ring silicone elastomers

The modified slide-ring cross-linkers were pre-cured in toluene with hydride terminated PDMS and chain extenders before solvent casting and final curing (see preparation scheme in Figure 6). The extent of the pre-curing reaction was found to be essential for ensuring a homogeneous reaction mixture in the final curing of the elastomer films. Insufficient pre-curing caused the formation of cross-linker rich domains (visible by the naked eye), while excessive pre-curing resulted in overabundant gelling in the casting solution that caused complications in obtaining even film geometries. Given the large molecular weight of the slide-ring cross-linkers ($M_n = 230\,000\text{ g mol}^{-1}$), longer linear PDMS segments were necessary to ensure that the polyrotaxane weight fraction would not be dominant in the curing formulations. Chain extenders were utilized to increase the length of the PDMS segments to approximately $64\,000\text{ g mol}^{-1}$, resulting in

Figure 5: A) Synthesis of modified polyrotaxanes with vinyl functional rings (ViPR). B) Vinyl groups per α -CD ring based on the feed ratio C) Fixed cross-links forming on the α -CD rings versus freely sliding network.

Figure 6: Synthesis of slide-ring silicone elastomers

Table 2: Dielectric and mechanical properties of sliding films.

	Polyrotaxane wt%	r	Y _{5%} MPa	Tensile strength MPa	ε' @0.1 Hz	ε' @1 MHz	tan δ @0.1 Hz	E _b V/μm
	9.4	1.5	0.529	0.75	2.7	2.8	8.8 · 10 ⁻²	59.0
	10.6	2.0	0.520	0.70	2.5	2.5	3.5 · 10 ⁻²	65.5
	14.8	2.5	2.017	0.77	2.6	2.7	1.2 · 10 ⁻¹	54.6
	17.3	3.0	2.962	0.94	2.8	2.8	3.2 · 10 ⁻²	56.3
	19.4	3.5	5.251	1.16	3.0	2.9	1.7 · 10 ⁻²	49.3
PDMS Control	0	1.5	0.192	5.46	3.3	3.3	8.0 · 10 ⁻²	39.5
Sylgard 184	0	NA	1.597	7.09	3.2	3.1	2.0 · 10 ⁻²	113.4

Figure 7: Tensile properties of sliding silicone films with differing cross-linker concentrations. Strain is defined as $(L - L_0)/L_0$ where L is the distance between the clamps during stretching and L_0 the initial separation distance.

silicone compositions of 81 to 91 weight percent without compromising the stoichiometric balance between the cross-linking functional groups. The stoichiometric balance between the sliding cross-linkers and the silicone component was controlled by the ratio between the vinyl groups of the modified polyrotaxanes and the hydride end-groups of the linear PDMS (Equation 1).

$$r = \frac{[\text{vinyl}]}{[\text{hydride}]} \quad (1)$$

The cured elastomers were transparent, and no visible phase separation was observed under optical microscopy.

3.3 Characterization of sliding silicone elastomers

A series of sliding silicone samples was fabricated with various cross-linker concentrations. The elastic modulus, taken as the slope of the stress-strain curves at 5% strain, ($Y_{5\%}$) of the elastomers increased in line with the cross-linker loading while still exhibiting strains at break of over 200% (as seen in Figure 7). The sliding samples with a lower cross-linker fraction ($r = 1.5$ and 2.0) had significantly lower elastic moduli compared to the commercial silicone elastomer reference sample. None of the sliding samples exhibited considerable strain hardening and maintained a stable stress-

Figure 8: Mechanical properties of the slide-ring networks. A) LVE study of the sliding transition for different cross-linker concentrations. B) Tensile properties of $r = 1.5$ sample at different strain rates ($L_0 = 20$ mm). All measurements conducted at room temperature.

1 strain slope after the initial inflection point. The tensile
2 strength of the samples did not vary significantly between the
3 samples with a lower *r*-value of 1.5 to 2.5, but increased
4 incrementally at higher ratios (Table 2).

5 All glass transition temperatures of the sliding samples fell
6 below the -90 °C limit of the analytical setup used.

7 The dielectric properties of the sliding silicone elastomers
8 were almost identical to the pure PDMS control sample
9 (Table 2). No significant change in dielectric permittivity (ϵ')
10 or dielectric loss tangent ($\tan \delta$) was observed with increasing
11 cross-linker fractions. This can be contributed to the change in
12 dielectric properties of the polyrotaxane cross-linkers after
13 chemical modification. The substitution of the polar hydroxyl
14 groups on the threaded cyclodextrin rings effectively lowers
15 both the permittivity and dielectric loss of the polarotaxanes
16 cross-linkers resulting to yield properties with great similarity
17 to PDMS. The dielectric breakdown strength (E_b) of the
18 sliding samples was considerably lower than the commercial
19 control sample, but this decreased value is most likely due to
20 the absence of reinforcing silica fillers in the prepared
21 formulations.

22 3.4 Time dependent behavior and sliding transition

23 The rheological properties of the sliding silicone
24 elastomers were studied by linear viscoelastic analysis to get
25 an understanding of the relaxation mechanisms within the
26 networks. A distinct transition in the storage modulus was
27 observed for the three sliding samples with a lower cross-
28 linker concentration ($r = 1.5$ to 2.5) around a frequency of
29 0.01 Hz (Figure 8A) (in other words a relaxation time of
30 approximately 100 s). This time dependent transition is
31 credited to the onset of ring sliding. Thus, the sliding entropy
32 of the rings dominates the elastic response of the elastomers at
33 slower operational speeds. This phenomenon is not common
34 in conventional elastomers, as seen for the PDMS control
35 sample. The frequency range of the transition was not
36 significantly affected by the cross-linker concentration, which
37 indicates that the time-scale is not affected by the stiffness of
38 the elastomers within the given range of samples. Rather we
39 hypothesize that a certain degree of relaxation within the
40 polyrotaxane needs to take place before free sliding is
41 possible. This phenomenon has been previously observed in
42 slide-ring hydrogels that exhibit a time-dependent transition
43 between a rubbery and sliding state [31]. To our knowledge, a

similar transition has not been reported for dry slide-ring
elastomers to date.

No transition could be observed in the two samples with a
higher cross-linker concentration (samples $r = 3.0$ and $r = 3.5$).
The absence of ring sliding could be due to the stiffening
effect of the high cross-linker loading suppressing the slope of
the transition. Higher polyrotaxane weight fractions in the
curing formulations have been found to have a reinforcing
effect on the cured elastomers that is independent from
concentration of networking groups (Table S1). The
reinforcing effect is also considered to be responsible for the
significant increase in elastic modulus of the samples with a
higher cross-linker concentration.

The time-dependent properties of the sliding elastomers
were confirmed by extensional rheology. No significant
change in elastic modulus or stress strain profile could be
observed when extension rate was decreased from 200 to
 20 mm per minute ($L_0 = 20$ mm). However, the modulus drops
significantly by half from 0.6 to 0.3 MPa, when the rate is
lowered to 1 mm per minute or less (Figure 8B). This type of
strain rate dependent phenomena is not present in
conventional elastomers (Figure S4).

The average Hencky strain rate (defined as
 $\dot{\epsilon}_H = (dL/dt)/L$) was determined to compare the time-scale
of the extended samples with the sliding transition observed in
the LVE study. The calculations confirm that the samples with
the stiffer elastic response were extended faster ($\dot{\epsilon}_H = 0.05$ to
 0.40 sec⁻¹) than the sliding threshold while the softer samples
were extended at rate below the sliding transition ($\dot{\epsilon}_H = 0.004$
and 0.003 sec⁻¹).

The results affirm the existence of two distinct modes of
behavior depending on if the threshold for sliding has been
crossed. This presents the potential to design smart dielectric
elastomer transducers with two distinct actuation responses
determined by the operational speed of the system.

To evaluate the actuation potential of the novel sliding
silicone films, the figure of merit (F_{om}) was calculated based
on Equation 2 where ϵ_0 is the vacuum permittivity. The
expression for the figure of merit was developed to present a
single parameter to directly compare the actuation
performance of different materials [32].

$$F_{om} = \frac{3\epsilon'\epsilon_0 E_b^2}{Y} \tag{2}$$

Table 3: Actuation comparison for sliding silicone elastomers (SSE).

	$Y_{5\%}$ MPa	ϵ' @0.1Hz	E_b V/ μ m	Actuation strain by area (%)	F_{om}
SSE	0.308*	2.7	59.0	20.3	0.81
Sylgard 184	1.597	3.2	113.4	17.5	0.68
Ecoflex 00-30	0.306	3.4	42.7	21.8	0.52
PDMS Control	0.192	3.3	39.5	30.4	0.71

*Elastic module of SSE when the strain rate is lower than the inverse sliding transition time

The sliding silicone elastomers were compared with commercial silicone elastomers, Sylgard 184 and Ecoflex 00-30, that are commonly used for fabricating actuating devices. Furthermore, simple actuation tests were conducted with all of the samples. Samples were pre-strained by 20% and actuation tests were conducted by applying a voltage on the samples at intervals of increasing strength (at 500 V steps) until breakdown. The actuation strain was measured by video analysis.

The figure of merit values and maximum actuation strain of the samples can be seen in Table 3. The sliding actuators exhibited increased actuation at lower voltages and a moderate increase in F_{om} when compared to the reference samples. The sliding elastomers performed considerably better in regards to breakdown strength when compared to the softer Ecoflex 00-30. The PDMS control sample resulted in the best actuation performance but it was obvious that the elastomer suffered from hysteresis. These initial results indicate the potential of the sliding system as a versatile platform for preparation of soft DEAs with improved crosslinking compared to commercially available soft elastomers based on low crosslinking densities, such as Ecoflex 00-30.

4. CONCLUSION

In summary, vinyl functional polyrotaxane cross-linkers were produced with commercially available precursors. The novel cross-linkers are soluble in common solvents and can be cured by conventional techniques, thus increasing their processability by industrially scalable methods and allowing them to be incorporated in silicone elastomer systems. This opens up the possibility to explore a new class of slide-ring silicone elastomers. The sliding silicone films had a well-defined network structure and exhibited two distinct time-dependent elastic responses that could be observed by both linear viscoelastic analysis and extensional rheology.

Acknowledgements

This work was supported by DTU's alliance stipend program.

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