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Published in:
Electroactive Polymer Actuators and Devices (EAPAD) XXII

Link to article, DOI:
10.1117/12.2557355

Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
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Jakob-Anhtu Tran, Jeppe Madsen, Anne Ladegaard Skov, "Utilizing slide-ring cross-linkers in polysiloxane networks for softer dielectric elastomer actuators," Proc. SPIE 11375, Electroactive Polymer Actuators and Devices (EAPAD) XXII, 1137518 (22 April 2020); doi: 10.1117/12.2557355

Event: SPIE Smart Structures + Nondestructive Evaluation, 2020, Online Only, California, United States
Utilizing slide-ring cross-linkers in polysiloxane networks for softer
dielectric elastomer actuators

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ABSTRACT

Slide-ring elastomers have mobile cross-links that can slide on their axial polymers in a manner similar to a pulley on a zip line. This supramolecular network structure imparts unique mechanical properties to the elastomers, such as high deformability and low hysteresis upon cyclic loading, that are often favorable for dielectric elastomer actuators (DEAs). The utilization of this type of dynamic network for actuation has been limited by the low compatibility of slide-ring materials and common elastomer platforms used in DEAs. Here, a synthetic pathway is proposed to allow for incorporation of slide-ring cross-linkers into silicone networks.

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

1. INTRODUCTION

Dielectric elastomer actuators (DEAs) have garnered considerable interest due to the possibilities they present as lightweight, flexible energy transducers with fast response rates. The applications for this type of innovative actuator range from soft robotics and artificial muscles to self-cleaning surfaces.¹ Silicone elastomers are commonly used for DEA fabrication because of their advantageous properties for actuation, such as a broad operating temperature, low mechanical loss, and biocompatibility.² When tailoring silicones for improved actuation at low voltages, two specific properties are sought after: high dielectric permittivity and low Young’s modulus. However, formulating softer elastomers from traditional curing schemes usually presents a tradeoff with lower mechanical integrity and higher viscous loss.³

As an alternative to common elastomers, slide-ring materials demonstrate a novel type of network structure in which, instead of traditional fixed cross-links, the junctions can slide on a molecular level, enabling a unique mechanical behavior often described as the pulley effect.⁴ When slide-ring materials are deformed, the sliding cross-links are able to dissipate the internal stress in a similar fashion to a pulley sliding on a rope. This molecular scale phenomenon has been credited for the softness and high maximum elongation of slide-ring elastomers.⁵ Additionally, slide-ring elastomers have been proven to exhibit low mechanical hysteresis, which has been attributed to the sliding cross-links’ ability to easily shift back to their relaxed state in a manner similar to a one-dimensional air spring.⁶

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. The supramolecular necklace structures form spontaneously when the PEG axis polymers and α-CD rings are dissolved in water. It has been found that the threading process is largely driven by hydrogen-bond formation between rings aligned by the axis polymer.⁷,⁸ The threaded complexes are then further stabilized by the formation of ordered hexagonal packing structures with neighboring molecules, which causes the aggregates to precipitate.⁹,¹⁰ Subsequent capping of the axis polymers with bulky stopper groups is then necessary to avoid dissociation of the rings and to form the final polyrotaxanes.

In order to create slide-ring materials, it is crucial that the polyrotaxane rings can slide freely on their axis polymers, which is not possible if they are densely clustered in crystalline domains. Disruption of the hydrogen bonding between the rings is thus necessary to enable their free axial movement. This disruption is generally achieved by substituting the hydroxyl groups on α-CD rings.¹¹ It is also possible to increase the solubility of the modified polyrotaxanes in common...
organic solvents by altering the substitution chemistry. The modified rings can then be linked together to form a sliding network.

While the production of PEG/α-CD polyrotaxanes has reached a commercial scale, their inclusion in silicone networks has been limited. Here, we have proposed a synthetic pathway to produce polyrotaxane cross-linkers that contain vinyl groups, allowing them to be incorporated into polysiloxane networks through hydrosilylation. This type of curing chemistry is commonly used in silicone elastomers due to its high efficiency and selectivity.

2. EXPERIMENTAL

2.1 Materials

Polyethylene glycol (PEG 35000) was purchased from Fluka. 1H-Benzotriazol-1-yloxytripyrrolidinophosphonium Hexafluorophosphate (PyBOP) was purchased from Tokyo Chemical Industry Co., Ltd. 1,3-divinyl-1,1,3,3-tetramethyldisilazane, platinum-divinyltetramethyldisiloxane 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. All other chemicals were purchased from Merck KGaA and used as is unless otherwise stated.

2.2 Characterization

$^1$H-NMR spectra were acquired on a Bruker 300 MHz spectrometer in either deuterated DMSO or chloroform at ambient temperature unless stated otherwise, with the residual solvent 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 Ulstrastyrage 10 Å column.

Thermogravimetric analysis (TGA) was performed in air with a heating rate of 10 °C min$^{-1}$ from RT to 900 °C on Discovery TGA instrumentation from TA Instruments. The onset of thermal degradation (T$_{5\%}$) was determined as the temperature at 5% weight loss.

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)). 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.

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 10 mm. The test specimens were elongated uniaxially at 50 mm min$^{-1}$.

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$^{-1}$–10$^{6}$ Hz. The samples were approximately 0.1 mm thick and 20 mm in diameter.

2.3 Preparation of polyrotaxanes

To prepare the carboxylic acid terminated PEG-COOH, ten grams of PEG was oxidized in 100 mL of DI water with 2,2,6,6-tetramethyl-1-piperidinyl radical (TEMPO, 100 mg, 0.64 mmol), KBr (116 mg, 0.97 mmol) and NaClO (20 mL, 5% available chlorine) at a pH of 11-12 for 15 min. The oxidation was quenched with 10 mL of ethanol. The reaction mixture was then acidified with HCl to a pH below 2. The product was extracted with two 100 mL aliquots of DCM that were then combined and evaporated in vacuo. The product was dissolved in hot ethanol and precipitated at -20 °C. The precipitate was then washed with ethanol and dried in vacuo overnight. The end-group conversion was confirmed with $^1$H-NMR to be >98%.

3 grams of PEG-COOH and 13.7 grams of α-cyclodextrin (α-CD) were dissolved in 100 mL of DI water and stirred for 15 minutes before overnight complexation at -5 °C. The complexed pseudo-polyrotaxane (PPR) was then freeze-dried and crushed into a fine powder. The PPR was then end-capped with the addition of 1-adamantylamine (169 mg, 1.1
mmol), PyBOP (581 mg, 1.1 mmol) and N, N-diisopropylethylamine (0.2 mL, 1.2 mmol). The mixture was dissolved in 100 mL of dry N, N-Dimethylformamide (DMF) and stirred overnight at RT in an inert atmosphere. The reaction mixture was then washed through centrifugation, twice with a 1 to 1 mixture of DMF/methanol and twice with methanol. The obtained solid was then dissolved in dimethylsulfoxide and precipitated in water, followed by repeated washing with water and freeze-drying.

2.4 Preparation of vinyl functional polyrotaxanes (ViPR)

The polyrotaxane material (1 g) was dissolved in dry DMSO (40 mL). A mixture (4.4 g, 20.4 mmol) of 1,3-divinyl-1,1,3,3-tetramethylsilazane (DVTMDS) and 1,1,1,3,3,3-hexamethylsilazane (HMDS) was slowly added to the reaction vessel in a drop-wise manner. The ratio of the silylating agents was varied between experiments. The reaction mixture was stirred for 6 hours at 60 °C, followed by an addition of dry THF (40 mL). The mixture 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.

2.5 Preparation of slide-ring silicone films

Hydride terminated PDMS (0.14 g, $M_n = 24,000$ g mol$^{-1}$), vinyl terminated PDMS extenders (0.06 g, $M_n = 20,000$ g mol$^{-1}$) and ViPR cross-linkers (0.04 g, $f_{vinyl} = 0.49$ mmol g$^{-1}$) were dissolved in Toluene. Platinum catalyst was added (50 ppm) and the mixture was left to pre-cure for 15 minutes at 80 °C. The mixture was then cast into a Teflon mold and left to evaporate for two days before the final overnight curing at 80 °C in an oven.

3. RESULTS AND DISCUSSION

3.1 Preparation of 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$^{16}$, with minor modifications. End-capping and purification of the complexed PEG and α-CD were confirmed by size exclusion chromatography. $^1$H-NMR was then used to determine the average number of α-CD rings threaded for each PEG chain (Figure 1). Approximately 100 rings were threaded for each polyrotaxane molecule, which corresponds to an inclusion ratio of 25%.
The polyrotaxanes were then modified to disrupt the dense packing structure of the rings and to improve their solubility in organic solvents while also introducing reactive handles for network formation. The hydroxyl groups on the α-CD rings were silylated with different feed ratios of HMDS and DVTMDS to control the number of reactive vinyl groups introduced per ring (Figure 2). An average of one networking group per ring is crucial to ensure that the cross-links can slide in relation to each other instead of forming fixed junctions on a single ring.
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 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 chloroform, toluene, and tetrahydrofuran.

Table 1: Effect of the feed ratio of the silylating agents on the final functional group composition of the modified polyrotaxanes (ViPR), where TMS is the unreactive trimethylsilyl group, OH the hydroxyl, and DS the degree of substitution of each glucose unit in the ring.

<table>
<thead>
<tr>
<th>Feed</th>
<th>Vinyl</th>
<th>TMS</th>
<th>OH</th>
<th>DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>12.9</td>
<td>5.1</td>
<td>2.15</td>
</tr>
<tr>
<td>0.25</td>
<td>0.6</td>
<td>12.0</td>
<td>5.3</td>
<td>2.11</td>
</tr>
<tr>
<td>0.35</td>
<td>1.0</td>
<td>10.5</td>
<td>6.6</td>
<td>1.91</td>
</tr>
<tr>
<td>0.51</td>
<td>2.1</td>
<td>11.2</td>
<td>4.7</td>
<td>2.21</td>
</tr>
<tr>
<td>0.73</td>
<td>5.3</td>
<td>8.1</td>
<td>4.6</td>
<td>2.24</td>
</tr>
<tr>
<td>1</td>
<td>11.0</td>
<td>0</td>
<td>7.0</td>
<td>1.83</td>
</tr>
</tbody>
</table>
3.2 Preparing 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 (Figure 3). 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 macroscopic phases, while excessive pre-curing resulted in issues during the casting process due to excessive gelling.

![Figure 3: Synthesis of slide-ring silicone elastomers.](image)

The cured elastomers were transparent, and no visible phase separation was observed under optical microscopy. Given the large molecular weight of the slide-ring cross-linkers ($M_n = 230,000$ g mol$^{-1}$), longer linear segments were necessary to ensure that the silicone component of the system would dominate the bulk dielectric properties. Chain extenders were utilized to increase the length of the PDMS segments to approximately 64,000 g mol$^{-1}$, resulting in the final composition of the network being 83 wt% silicone.

The mechanical and dielectric properties of the slide-ring elastomer are shown in Table 2. The dielectric permittivity and electrical breakdown strength of the films were in the same value range as pure silicone elastomers, confirming the negligible effect of the cross-linkers on the bulk properties. The Young’s modulus and maximum strain of the initial slide-ring elastomers presented no improvement compared to commercial silicones. This could be caused by the formulation of the curing mixture resulting in a denser network. Alternatively, the high number of threaded rings on each axis polymer could also restrict the degree of molecular sliding possible for the rings. Further study of different curing compositions and fixed cross-linked analogues is thus necessary to confirm the intrinsic properties caused by the ring sliding.

<table>
<thead>
<tr>
<th>Y (MPa)</th>
<th>$\varepsilon'$</th>
<th>$E_b$ (V/µm)</th>
<th>Max. strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7</td>
<td>2.6</td>
<td>37.8</td>
<td>250%</td>
</tr>
</tbody>
</table>

3.3 Thermal properties of the slide-ring materials

Thermal degradation studies on the polyrotaxane materials and precursors revealed that modifying the hydroxyl groups increased the thermal stability of the polyrotaxanes (Figure 4). Substituting the hydroxyls with silyl groups increased the onset of thermal degradation by 13%, while grafting polysiloxane side-chains showed an increase of 64% compared to the unmodified polyrotaxanes. However, the cured slide-ring silicone film had a slightly lower thermal stability when compared to the grafted rotaxanes.
4. CONCLUSION

Homogeneous silicone slide-ring elastomers were successfully synthesized by modifying PEG and α-CD based polyrotaxanes to facilitate curing with linear polysiloxanes. The modification method allowed control of cross-linking functionalities per threaded CD rings and was found to increase the thermal stability of the polyrotaxanes. The dielectric properties of the slide-ring elastomers were shown to be dictated by the silicone component of the material. A wider study of the chemistry of the linear part of the network and the inclusion of reinforcing fillers would be required to fully explore the mechanical effect of ring sliding in these novel elastomers as well as their further use as dielectric elastomer actuators.
5. REFERENCES


