

Synthesis of Liquid Crystal Elastomer Threads for the Creation of Self-Tying Knots

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ABSTRACT

The objective of this study is to create Liquid Crystal Elastomers (LCEs) strands for potential applications in the development of knot-based actuators. LCEs are novel polymers that combine elasticity inherent in traditional elastic polymers with the self-organizing attributes of liquid crystals. This unique combination allows these polymers to both hold the shape they are stretched to and actuate (retract to their original shape) in response to outside stimuli, notably heat and light. Different synthesis methods and formulations for LCEs yield varying material properties, including transition to nematic-isotropic phase (TNI), stiffness, and actuation force. Achieving a delicate balance among these properties is pivotal for engineering LCE strands capable of autonomously self-tightening into knots. This investigation explores two distinct approaches for fabricating LCE strands: the one-pot method and the oligomer method. Furthermore, it studies the influence of additives, such as carbon nanotubes (CNTs), cellulose nanocrystals (CNC), and graphene oxide (GO), on the efficiency and effectiveness of LCE strand actuation, with a particular focus on self-tightening behavior. The use of CNTs and the one-pot method showed great promise in the characterization tests of the samples. The samples had a high responsivity and low TNI in comparison to other recipes tested, which allowed for the creation of responsive strands that are capable of self-tightening when the right knot geometry is used.

(Note: This paper was written for a high school class.)

INTRODUCTION:

The use of soft-robotics and smart polymers for use in medical application is a recent branch of engineering and materials science. Liquid Crystal Elastomers (LCEs) are one of many novel materials that have the ability to actuate and hold shape memory. This means that they have the ability to be deformed, hold their deformed shape, and then retract when an outside stimulus is applied, which is usually heat or light with LCEs (Aharoni et al., 2018).

In the expanding landscape of materials science, LCEs stand out as a class of polymers characterized as mesogens organized in a crystalline structure. Combining the elasticity reminiscent of elastomers, akin to a rubber band, with the ordered crystalline structure typical of liquid crystals, LCEs exhibit a remarkable phenomenon. Upon stretching, these materials transition into a nematic state, aligning their constituent crystals and storing potential energy within this alignment. Upon application of an external stimulus, these crystals revert to an isotropic state, where alignment is lost. Interestingly enough, this is evident in LCE samples, as when they are stretched, they often turn transparent, indicating that their crystals have been aligned, as shown in *Fig. 1* (Guin et al., 2018).

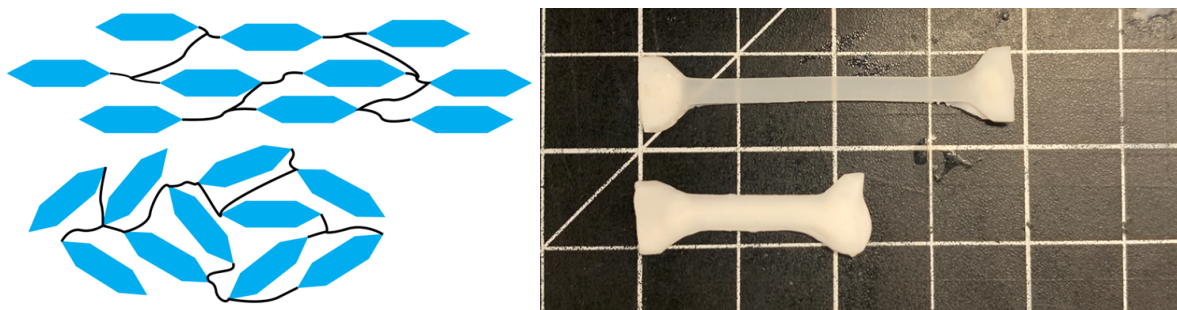


Figure 1: Nematic (top) vs. isotropic (bottom) state of a LCE

The exceptional actuation property of LCEs has generated considerable enthusiasm within the scientific community. Not only can the actuation of LCEs be controlled, but these materials can also be programmed into predetermined shapes. Engineers are working to use

LCEs for a large range of applications, from biomimetic materials and tissue engineering to various feedback sensors (Wang et al., 2022). Employing various mold shapes and UV curing techniques, researchers have been able to program LCEs into intricate shapes, such as faces, and even made LCEs fold like origami. Moreover, they have been able to produce movement using LCEs (Aharoni et al., 2018). The programmability of this material means that researchers have great control over the functionality of the LCEs.

Researchers have delved into the potential of LCE strands, which exhibit actuation even under relatively modest loads, enhancing their versatility and potential utility across a spectrum of applications (He et al., 2021). Others have conducted experiments to actuate LCE strands through various means, such as heat, light, and toluene vapors, unveiling an intriguing auto-untie action, which contrasts with the intended objectives of this research (Liu et al., 2021). Despite this, this research can still be applied to the goal of creating a tightening as it is evidence of friction not playing a substantial obstacle in knot movement.

While other researchers have developed elastic shape-memory polymers for similar applications (Lendlein & Langer, 2002), the unique tunability of the transition-to-isotropy temperature (TNI) and other essential characteristics make LCE research particularly promising. By modifying the method of crystalline structure production within LCEs and incorporating various additives, the properties of LCE strands can be finely tuned. Drawing from research in knot geometry and physics, the knot geometries within LCEs can be optimized for specific applications (Johanns et al., 2023).

This research aims to create LCE strands that exhibit effortless actuation and self-tightening upon exposure to light. Our investigation involves exploring diverse approaches to synthesize the crystal structure, including the one-pot method and the oligomer method, along

with experimentation with various additives such as CNTs, CNC, and GO. Ideally, the LCE strands have a low TNI, are capable of actuating using IR light, have a strong actuation force, and have a relatively strong tensile strength.

METHODS:

Production of the One-Pot Methods:

The synthesis of one-pot polymers commenced by dissolving RM82 monomer in toluene within a vial, at a constant temperature of 90°C within an oven. After the solution was homogenous, chemicals EDDT, PETMP, and HHMP were added and dissolved, heated again to 90°C. After being thoroughly mixed, the solution was cooled to room temperature. Any desired additives were incorporated into the mixture at this point. DPA dissolved in toluene in a 1% w/w solution was added and mixed using a vortex mixer. The solution was poured into a silicone mold and let to sit overnight in a UV light-free environment. To form strands, the solution was drawn into a syringe and injected into a tube, which was placed in a UV light-free environment.

After an overnight curing process, the solidified polymer was carefully removed from the mold and subjected to a 90°C oven to facilitate the evaporation of residual toluene. The amounts of the various chemicals are detailed in *Table 1*, depending on the desired dicell to thiol ratio.

Chemical	1:1	1:1.4	1:1.8	1:2.2
RM82	2 g	2 g	2 g	2 g
Toluene	0.62 g	0.62 g	0.62 g	0.62 g
EDDT	0.111 g	0.1555 g	0.1999 g	0.2443 g

PETMP	0.5952 g	0.8333 g	1.0714 g	1.3095
HHMP	0.00472 g	0.00472 g	0.00472 g	0.00472 g
DPA	0.00648 g	0.00648 g	0.00648 g	0.00648 g

Table 1: Quantities of chemicals used in the one-pot method depending on desired dicell:thiol ratio

Production of Oligomer Method

10g of RM257 monomer was dissolved in 125mL of Methylene Chloride in a round bottom flask. On the side, a solution of EDDET and 4 drops of DBU were mixed thoroughly. The amount of EDDET depended on the RM257 to EDDET molar ratio desired, as outlined in *Table 2*. The solution was added to the flask in small increments over around 2 minutes. The combined solution was stirred using a stir bar and covered with tin foil for 16 hours to minimize evaporation of the solution. The solution was moved to a beaker and 0.1g of BHT was added and dissolved. The stir bar was removed, and the solution was heated in a fume hood at 90°C for 12 hours, yielding a highly viscous liquid, referred to as the oligomer. The oligomer was stored in a refrigerator until it was required for use.

RM257:EDDET Molar Ratio	EDDET Mass (g)
1.02:1	3.036
1.10:1	2.816
1.15:1	2.693
1.20:1	2.581
1.25:1	2.478
1.50:1	2.060

Table 2: Quantity of EDDT for desired RM258:EDDET molar ratio

Approximately 2g sample of Oligomer was added to a vial heated in a 90°C oven to reduce its viscosity. 4% w/w methylene chloride and 2% w/w DMPA were added and mixed in. Any additives were also added at this stage. The oligomer was added to a syringe and an 18-gauge nozzle was attached. The syringe was covered with aluminum foil to prevent UV light from initiating crosslinking of the oligomer. The syringe was added to a syringe pump and extruded slowly to induce shearing on the oligomer. The nozzle was heated using a heat gun to allow for easier extrusion. The extruded strand was immediately cured using a UV light to crosslink the oligomer, utilizing the configuration depicted in *Fig. 2*. The strands were separated and placed under a UV light and cured until no longer sticky to the touch.

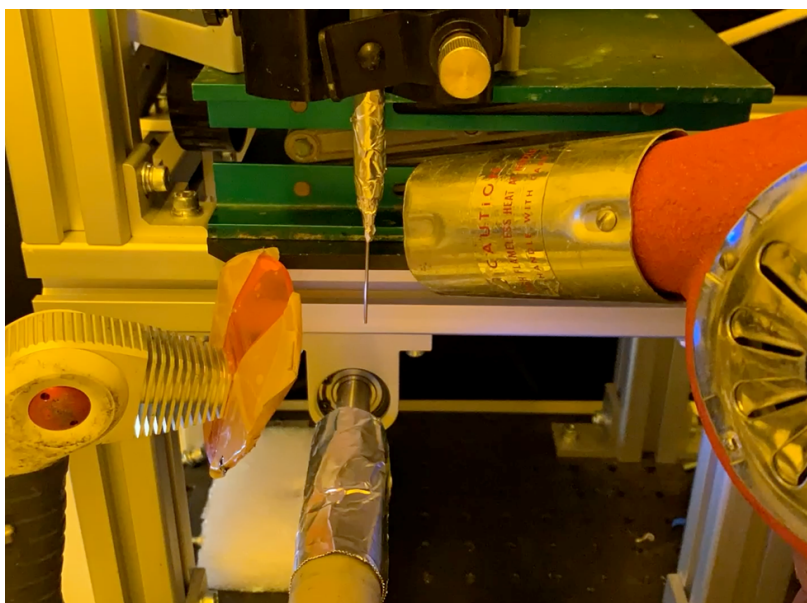


Figure 2: Oligomer method UV curing setup

One-Pot Characterization: Young's Modulus

A dogbone sample, as illustrated in *Fig. 1*, was placed in an INSTRON Universal Testing Machine, which measures the force on a load cell. The sample was stretched to the breaking

point to measure the force needed to stretch the sample. The data was plotted in a stress vs. strain graph.

One-Pot Characterization: TNI

A dogbone sample was stretched approximately 80% of its original length. The sample was placed on a white background. The sample was heated using an infrared light until full actuation was achieved. An infrared/temperature camera was used to record the temperature of the sample and the time needed to achieve actuation.

One-Pot Characterization: Knot Friction Force

A syringe needle was placed into the upper clamp of an INSTRON Universal Testing Machine. Using a lab beaker clamp and stand, a piece of plastic with a small hole the same diameter of the needle was placed right below the needle. The INSTRON was used to insert the needle into the hole. A strand of LCE was loosely knotted around the needle and the ends were clamped. The entire setup, depicted in *Fig. 3*, was used to measure the force required to retract the needle. The LCE knot was actuated using an IR light over a 2 minute period, tightening around the needle. The needle was retracted once more while the light remained on, with the force needed for retraction recorded. The two forces recorded were compared.

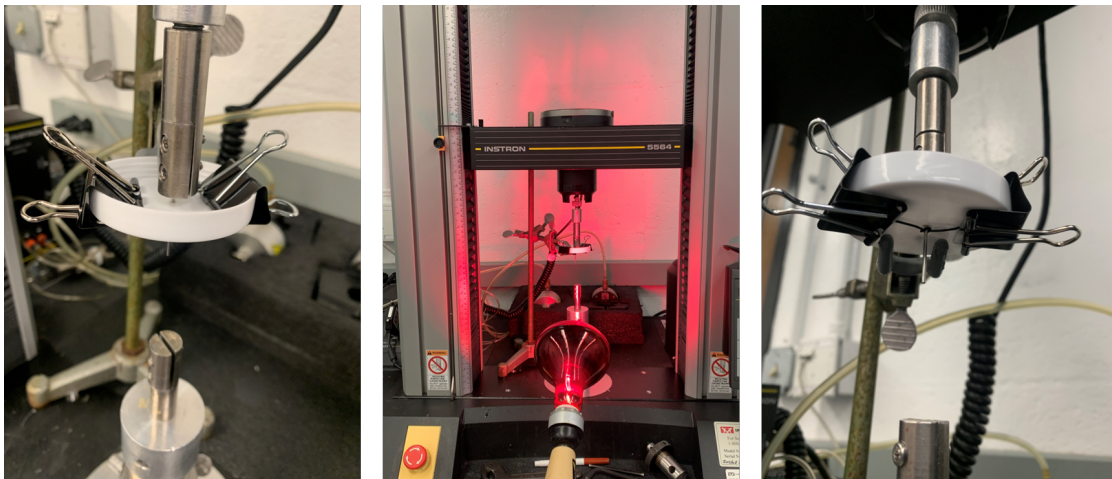


Figure 3: Knot friction force test setup

Materials:

- RM82 (1,4-Bis[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene)
 - RM257 (1,4-Bis[4-(3-acryloyloxypropyloxy) benzoyloxy]-2-methylbenzene)
 - EDDET (2,2'-(Ethylenedioxy)diethanethiol)
 - PETMP (Pentaerythritol tetrakis(3-mercaptopropionate))
 - HHMP (2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone)
 - DPA (Diphenylamine)
 - DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene)
 - BHT (Butylated hydroxytoluene)
 - DMPA (2,2-bis(hydroxymethyl)propionic acid)
 - Toluene
 - Methylene Chloride
 - CNC (Cellulose nanocrystals)
 - CNT (Carbon nanotubes)
 - GO (Graphene Oxide)
 - Silicon Molds (Smooth-On Ecoflex 00-50)
 - Disposable vials, pipettes, tubing
 - Glassware, hot plates, stands and clamps, etc.
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RESULTS:

Formula Experimentation:

Varying the chemical amounts in *Table 1* results in the change of the ratio of ends available to crosslink. More specifically, it changes the ratio of the ends of the RM82 to the thiol groups available. The larger the ratio, the more elastic and responsive the elastomer was, but also weaker with retraction strength. 1:1.18 was found to be the ideal ratio for the purposes of this experiment.

Adjusting the RM257 to EDDET ratio, as indicated in *Table 2*, changes the amount of crosslinking in the oligomer. With more EDDET, the more crosslinking there is in the oligomer. The more crosslinking there is the more responsive the strands were. However, the oligomer also became more viscous and difficult to extrude. The 1:1.15 ratio of RM257 to EDDET provided the most responsiveness with a possible extrusion.

Additives were added to both the One-Pot and Oligomer methods. The addition of GO and CNC did not have a noticeable effect on the actuation of either of the samples. CNTs had a noticeable effect on both the actuation speed and the responsiveness of the LCE to IR light.

By forming LCE strands into knots and clamping to two ends, the strands were able to tighten when actuated with IR light, as demonstrated in *Fig. 4*.

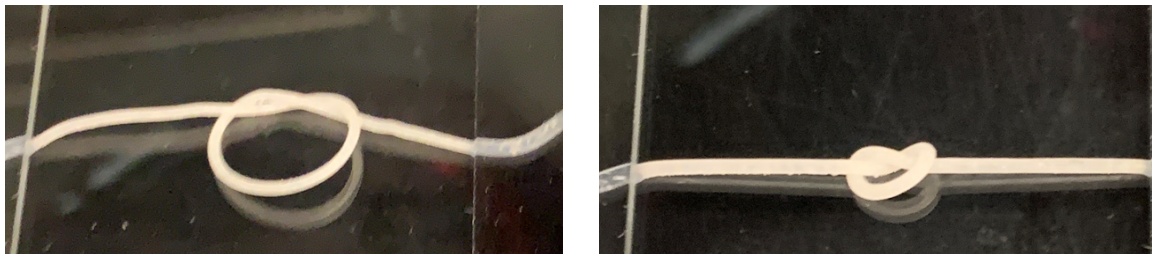


Figure 4: Before (left) and after (right) of IR light actuation of LCE strand

Plain vs CNT One-Pot Samples:

Using the 1:1.18 ratio One-Pot sample, the difference of tensile strength between a plain LCE and a sample with CNTs added was tested, as shown in *Fig. 5*. The Young's Modulus of the plain sample measured $1.239\text{E}+06$, whereas the CNT-infused sample registered a higher value of $1.582\text{E}+06$. This indicates that the CNT-infused sample is stiffer than the plain sample.

Moreover, the CNT-infused sample exhibited reduced elasticity compared to the plain sample, as it could not be extended to the same extent as the plain sample.

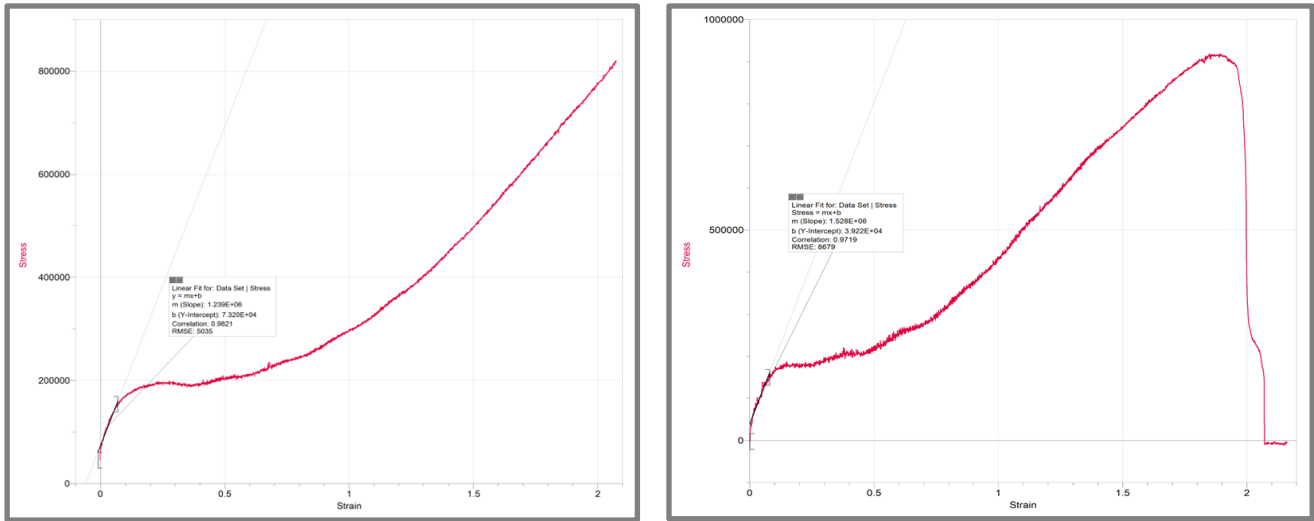


Figure 5: Young's Modulus experiment graphic comparing plain (left) to CNT (right) samples.

The CNT sample showed more responsiveness to IR light and also increased its temperature quicker. *Fig. 6* shows that the time it took the CNT sample to reach around 40 C (about the TNI) is much shorter than the plain sample.



Figure 6: TNI test setup, with plain sample (left) reaching TNI in a shorter time than the CNT (right) sample

As shown in *Fig. 7*, the CNT-infused samples also exhibited greater responsiveness in terms of actuation strength when exposed to IR light, in comparison to the plain samples. Notably, the friction experienced during actuation under IR light was significantly higher in the CNT samples than in the plain samples. Moreover, the initial friction in the CNT samples was also found to be higher than in the plain samples. Subsequently, when evaluating the residual knot force, it was observed that the CNT samples exhibited a lower force under IR light.

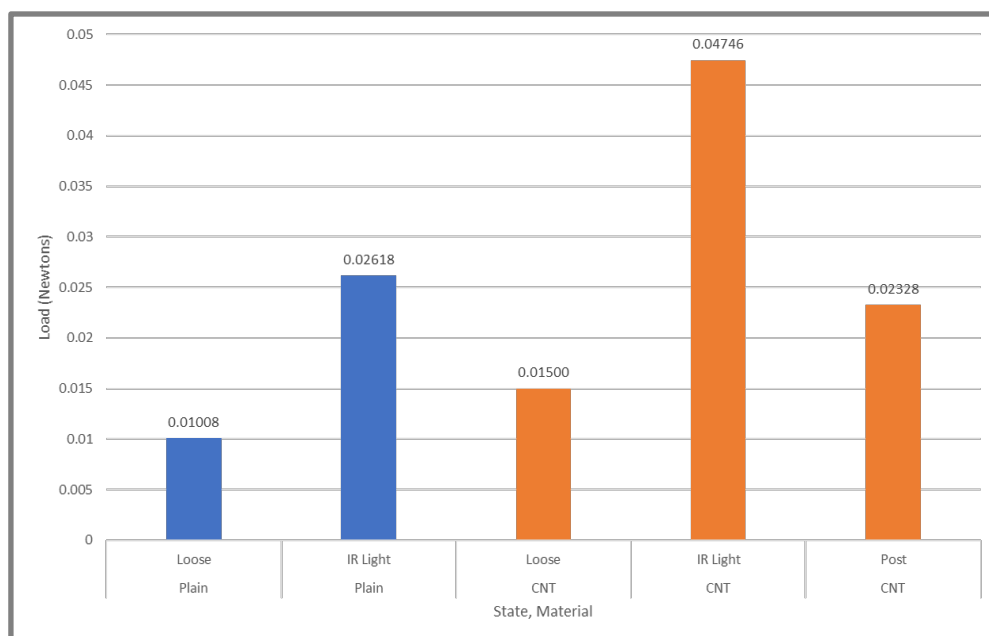


Figure 7: Knot friction test results

DISCUSSION:

Initial observations indicated that the most reactive One-Pot samples were those formulated with a ratio of 1:1.18. When the dicell to thiol group ratio is decreased, as seen in *Table 1*, it results in increased crosslinking, resulting in a less elastic LCE with enhanced actuation strength. Interestingly, the TNI temperature of the sample also experiences a significant increase with the reduced ratio, suggesting a higher energy requirement for actuation.

A similar principle applies when altering the RM257 to EDDET ratio in the oligomer method as seen in *Table 2*. Increased EDDET content leads to greater crosslinking, resulting in a more reactive but less elastic LCE strand. Furthermore, the extrusion of the strand becomes considerably more challenging with higher EDDET content in the formula, reinforcing the notion of increased crosslinking in the oligomer. While increased actuation strength is a desirable characteristic, the increased difficulty in extrusion necessitates a trade-off, potentially sacrificing the overall LCE quality for synthesis.

Comparing the synthesis methods, the One-Pot approach proves to be more manageable compared to the oligomer method, prompting its selection for all subsequent tests. Interestingly, the addition of GO and CNCs did not significantly alter the samples, despite the theoretical expectation of reducing the TNI and enhancing strand actuation. It's conceivable that the particle size was too large, leading to reduced effectiveness within the elastomer. Conversely, the addition of CNTs demonstrated remarkable effectiveness in reducing the TNI of the LCE samples. The CNTs' black color and shape enhanced heat absorption from infrared (IR) light, resulting in increased actuation efficiency in the samples.

The addition of CNT also changes other properties of the LCE as well. The CNT samples of LCE are more stiff and also less elastic, as indicated by the tensile strength test in *Fig. 5*. Additionally, the reduced TNI and actuation speed of the CNT sample is much more apparent when compared to the plain sample under and IR light, as seen in *Fig. 6*. As a result, the actuation force of the knots is also much higher in the CNT samples, which was also indicated in the knot friction test as seen in *Fig. 7*. These tests collectively highlight the suitability of LCEs for forming self-tying knots.

Through these efforts, we have honed in on an optimal recipe for producing LCE strands with the desired characteristics outlined above. We are hopeful for the application of these self-tightening strands for use in knot-based actuators. The proof of concept in *Fig. 4* indicates that these self-tying knots have potential applications with knot-based actuators. The convenience of utilizing infrared (IR) light for inducing movement is particularly promising. Much further research is warranted, not only to refine fabrication techniques and methods for these strands but also to explore formulations that enhance both tensile strength and actuation strength, while also rendering the strands more responsive to external stimuli. Additionally, more accurate and

quantitative tests to quantify the strands will be useful in comparing different formulas. Finally, experimenting with different knot geometries might allow for easier knot tightening and stronger knots.

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