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Untethered Recyclable Tubular Actuators with Versatile Locomotion for Soft Continuum Robots

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Stimuli-responsive materials offer a distinguished platform to build tether-free compact soft robots, which can combine sensing and actuation without a linked power supply. In the past, tubular soft robots have to be made by multiple components with various internal channels or complex cavities assembled together. Moreover, robust processing, complex locomotion, simple structure, and easy recyclability represent major challenges in this area. Here, it is shown that those challenges can be tackled by liquid crystalline elastomers with allyl sulfide functional groups. The light-controlled exchange reaction between allyl sulfide groups allows flexible processing of tubular soft robots/actuators, which does not need any assisting materials. Complex locomotion demonstrated here includes reversible simultaneous bending and elongation; reversible diameter expansion; and omnidirectional bending via remote infrared light control. Different modes of actuation can be programmed into the same tube without the routine assembly of multiple tubes as used in the past. In addition, the exchange reaction also makes it possible to use the same single tube repeatedly to perform different functions by erasing and reprogramming.

Compared to conventional robots composed of rigid materials with limited mobility, soft robots composed of deformable components can achieve versatile and continuum locomotion and manipulate objects with multiple degrees of freedom, which provide safer human–robot interaction and advantage in adapting to confined environments. Driven by both fast growing market-needs and widespread scientific interests, research on soft robots has been intensified over the past decade.[1] Tubular soft robots are of particular importance for their potential applications such as artificial blood vessels,[2] stents for intraluminal prosthesis or aneurysm treatment,[3] and catheters in minimally invasive surgery.[4] So far, typical tubular soft robots include cable systems[5] and inflatable structures driven by pressurized fluid (gas or liquid).[6] For those robots to work, they have to have a tether such as a battery, steering wire, or pneumatic power supply. The use of a tether poses serious limit in their applications. For example, it is hard to place and control robots in distant and dangerous areas that are not fit for human to enter. Stimuli-responsive materials provide a unique solution to fabricate untethered soft robots. In practice, soft robots made of shape-memory alloys or magnetic actuator have been reported.[7] However, shape-memory alloys require very high operating temperatures while magnetic actuators have problems with portability and high cost of the external driving magnets or MRI machines. Moreover, none of previously reported tubular robots is entirely made of soft materials. To control the movements, rigid components such as metal wires or ponderous compressors have to be attached,[1c,6,8] which creates tremendous obstacle on the compact design and practical applications of soft robots. To make a tubular robot or actuator entirely with one soft material is a formidable challenge to the materials science community.

There are several other concerns on constructing tether-free tubular soft robots or actuators based on stimuli-responsive polymers. The first one is complex locomotion modes. The basic locomotion is usually bending or extension.[9] It is very difficult to control the tube to have complex movements such as reversible bending accompanied with extension, contraction/expansion of the tube diameter, and controllable omnidirectional bending. To achieve elaborate and accurate control, it is vital for tubular robots to perform sophisticated motions other than simple bending or extension. The second one is the assembly of tubes with different modes of locomotion. It is highly desirable to accomplish on-demand maneuverability for specific tasks. Meanwhile, different modes of locomotion might be required in different regions of one tube. For example, the one part of the tube would elongate to reach an object while the end of the tube would act as gripper to grasp the object based on the change of the tube diameter. To assemble several parts

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with different functions, either adhesive or mechanical linkages have to be used to bond them together conventionally. As a result, not only the fabrication is complicated but also the possible leakage at the junctions of the tubes prevents the effective delivery of fluids. For the compactness of soft robots or actuators, it is best to use only a single material to build the tube with different modes of locomotion programmed on the same tube, but none of the current materials or techniques accomplished this. The third concern is the recyclability or reprogrammability. Once the tubes are fabricated, their modes of locomotion are fixed. They can only operate for a specific task. Oftentimes, other tasks may need only a little modification on the locomotion of the tube, but a totally new tube has to be fabricated from the very beginning of the tube preparation. It will be much easier and cost-effective to reprogram the tube for various tasks without disposal. In fact, the above challenges are also common problems faced by all the currently reported soft robots. Thus, suitable and flexible soft tubular actuators are urgently needed.

Here we demonstrate that, using one single liquid crystalline elastomer (LCE), we can make tether-free soft tubular robots/actuators, which can achieve designed complex locomotion, allow the same tube to have different locomotion in different regions and be reprogrammed to have new modes of locomotion again and again. LCEs are capable of large deformation upon the application of external stimuli, which can induce the liquid crystal-isotropic phase transition.[10] LCEs are especially suitable for soft robots.[1f,11] For example, LCE swimmers as microrobots[11b] have shown periodic and continuous self-propelling motion. However, in terms of tubular actuators made of LCE materials, there is only one example so far, where LCE capillaries were fabricated to mimic the motion of earthworms.[12] Similar to LCEs, linear liquid crystalline polymers can be processed into microfluid channels to control liquid flow.[13] Nevertheless, all these tubular LC actuators were tiny in scale and only realized basic locomotion. These tubular structures cannot address the above mentioned three challenges.

We here follow the ideas of liquid crystalline elastomers with exchangeable covalent links (adaptable LCEs). The main obstacle that prevents the fabrication of relatively larger LCE tubes with flexible locomotion lies in the difficulty to install heterogeneous alignment in different areas.[14] Macroscopic alignment is the key for actuation, but hard to achieve in covalently cross-linked LCEs.[11f,15] Since 2013, other researchers and we have started to build LCEs with exchangeable links, which provides a new method to align or adjust liquid crystalline networks after the formation of covalently cross-linked systems.[16] The exchangeable links reported in LC materials so far are based on ester,[16c,17] disulfide,[18] and allyl sulfide groups.[19] For networks with ester and disulfide groups, the exchange reactions are triggered by high temperatures, which can fix the alignment of the network under external force, but they can also diminish the alignment without external force. Allyl sulfide groups can add photoinduced plasticity into covalently cross-linked polymer networks.[20] When introduced into LC networks (LCNs), they make it possible to use light to erase the alignment obtained by polymerization in LC cells and implement delicate control of alignment and birefringence in ordered LCNs.[19] In that report,[19] the LC network is densely cross-linked and not used as actuators. However, that report suggests that if allyl sulfide groups are introduced into LCEs, the resulted alignment will be relatively stable when heated.

To make tubular actuators, we synthesized a new LCE with allyl sulfide groups in the backbone. We choose the monomers as illustrated in **Figure 1**a to synthesis LCE. RM 257 provides mesogens, DODT is the spacer, PETMP is the cross-linker, and MBTA is used to introduce allyl sulfide functional groups which can exhibit allyl sulfide exchange for the processing of actuators later. The polymerization is completed by thiol–acrylate click reaction to avoid harsh reacting conditions. The details of the synthesis are given in the Supporting Information. The crosslinking density of network can be regulated by the ratio of two thiol monomers. Considering the elasticity of networks and the arrangement of liquid crystal mesogens, we selected the molar ratio of DODT/PETMP as 20. Photoinitiators which can produce radicals upon UV irradiation to activate the exchange reaction of allyl sulfide groups are introduced into the reaction mixture before polymerization. Swelling experiment indicated that the network was covalently cross-linked (Figure S1, Supporting Information). Differential scanning calorimetry (DSC) showed that the resultant LCE had a LC-isotropic temperature (T_i) at about 40 °C (Figure 1b) upon heating. According to dynamic mechanical analysis (DMA), the glass temperature (T_g) was 4 °C and the modulus at room temperature was about 2.5 MPa (Figure S2, Supporting Information). The stress–strain curve (Figure S3, Supporting Information) revealed that the breaking elongation was ≈600%. All the above results demonstrated that the cross-linked network was soft with excellent elasticity.

Due to the presence of allyl sulfide groups, macroscopic alignment could be readily formed in LCE films after the film was synthesized. Allyl sulfide functional groups in the backbone of cross-linked LC networks are sensitive to free radicals.[19] Upon UV irradiation, photoinitiators produce radicals. Addition-fragmentation chain transfer (AFCT) between allyl sulfide functional groups is therefore activated.[20,21] This leads to a topological change of the network when external force is applied, so as to relax the stress all over the network. Consequently, when the film is stretched and exposed to UV light, macroscopic alignment of liquid crystal is established and remains after turning off the UV light. The aligned LCE (the so called monodomain LCEs[22]) contracted when heated to above the T_i and elongated by 45% when cooling down to below the T_i (Figure 1c). In Figure 1c, the high temperature we used was 50 °C. In fact, any temperature above T_i but below the degradation temperature (260 °C, Figure S4, Supporting Information) was suitable to trigger the actuation. The alignment of the LCE was also confirmed by 2D X-ray diffraction, which suggested a well-oriented nematic order (Figure 1d). Other demonstrations of the alignment in LCEs are given Figures S5–S7 (Supporting Information). The actuation strain was dependent on the prestrain of the film resulted from stretching with UV irradiation. As shown in Figure 1e, the actuation strain increased first with the prestrain, but it reached plateau when the prestrain was above 150%. We postulate that 150% is the minimum prestrain which is necessary to align all the mesogens. If the strain is smaller, not all mesogens can reach the best alignment. Additional prestrain above 150% makes no significant contribution

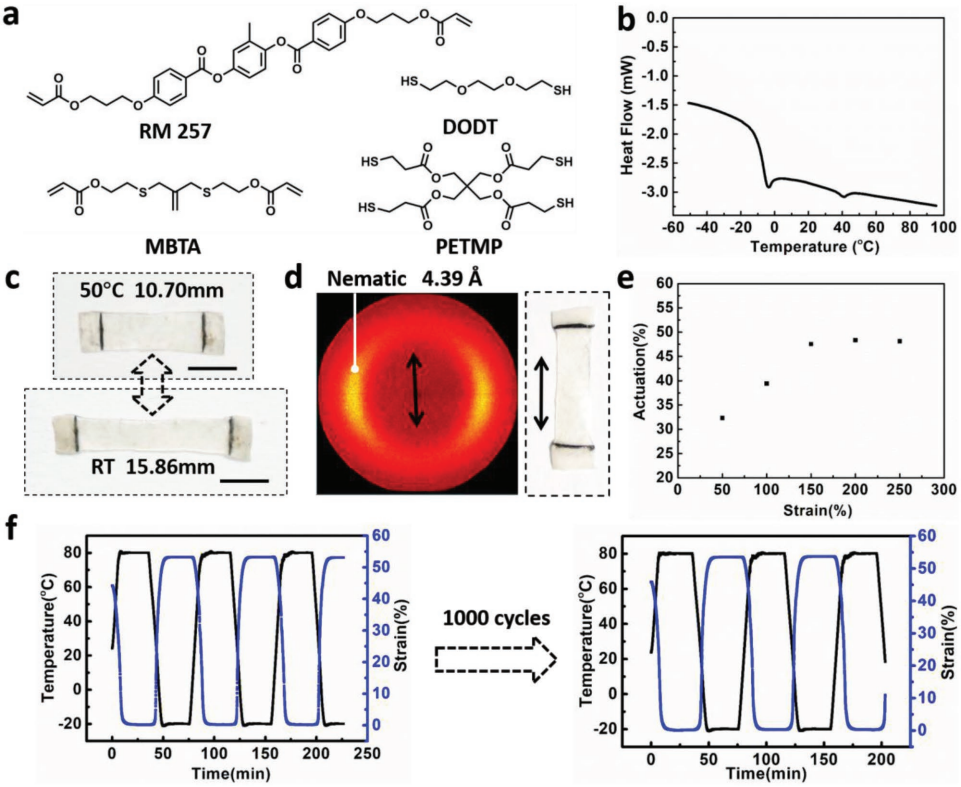

Figure 1. Synthesis of LCEs and actuation of monodomain LCE. a) Monomers used for the synthesis of LCEs. b) DSC curve of the LCE (second heating cycle, 10 °C min^{-1}). c) Thermal actuation of monodomain LCE. d) X-ray diffraction image of monodomain LCE. e) Strain–actuation scattering diagram of adaptable LCE. f) Repeated actuation of monodomain LCE. Scale bar: 5 mm.

to the alignment of mesogens and, therefore, the actuation strain reaches the observed plateau.

Compared to other LCEs with exchangeable links based on transesterification or disulfide, LCEs with allyl sulfide functional groups have distinct advantages in terms of stability. The monodomain sample showed an excellent repeatability of actuation even after 1000 cycles of heating and cooling as demonstrated in Figure 1f. It should be noted that it is important to remove the residual photoinitiators with extraction by swelling in solvents in order to keep them from generating unnecessary radicals during the heating–cooling cycles. As the photoinitiators were totally removed, the orientation can be maintained after swelling. As shown in Figure S8 (Supporting Information), the alignment of liquid crystals in AFCT-LCEs kept intact and reversible actuation was still observed after swelling in dichloromethane (DCM) and deswelling by natural drying.

The preparation of aligned tubular LCE is similar to that of the films. First, we made a tubular LCE without any alignment by injecting the mixture solution into a home-made mold. The rapidness and insensitivity to reacting conditions of thiol–acrylate click reaction simplified the fabrication of tubular structures and no high-temperature or high-pressure handling was required. To introduce alignment, the tube was stretched uniformly upon exposure to UV light, leading to a uniform orientation. Therefore, both the top and bottom sides had the same actuation property. The aligned tube showed 1D reversible change in length (**Figure 2**a) upon liquid crystal–isotropic phase transition. Reversible bending of tubular structures (Figure 2b) was achieved by irradiating only one side of the tube wall while the whole tube was stretched. Although the other side was also strained, it was not irradiated because light was obstructed physically by opaque strip placed through the tube. Consequently, the irradiated side was oriented and capable of elongation while the unirradiated side was still in the state of polydomain and remained the original length upon external stimuli. To accommodate the asymmetric elongation, the tube bends toward the aligned side upon heating. As shown in Figure 2b, the tube shows reversible bending and unbending upon temperature change. Similarly, "S" shape of tubular structure can be achieved by irradiating the top side of the left half and the bottom side of the right half under uniaxial tension (Figure 2c).

To achieve the complex motions of LCE actuators, inhomogeneity in alignment is the key factor. If the inhomogeneity in both the longitudinal and peripheral directions can be conveniently programmed, then various complex motions will be feasible. The reason why we choose light as external stimuli for alignment is that, as we have shown in the processing of bending and "S" tubes, light can be controlled and modulated readily to realize local programming at any specific region which is hard for heating to achieve. This adds great advantages to implement inhomogeneous alignment in the tube. As different kinds of inhomogeneity of alignment can be designed and produced, hollow 3D LC tubes can display reversible complex and combined deformations. As shown in Figure 2d, the tube demonstrates elongation and bending simultaneously.

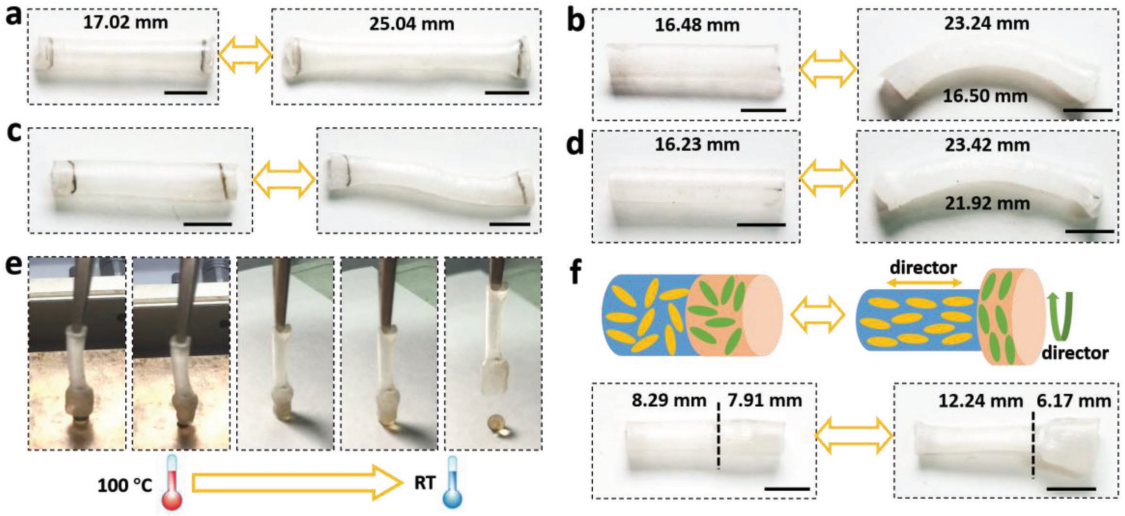

Figure 2. Demonstration of complex motions of the tubes. a) Reversible elongation. The overall strain of actuation is 47%. b) Reversible bending. The actuation strain of the top side is 41% and the bottom side has no change in length. c) The S-shape tubular actuators. The deformation is reversible responding to changes of temperature. d) Reversible simultaneous bending and elongation. The actuation of the top side and the bottom side is 44 and 35%, respectively. The overall tube shows the combined motion of elongation and bending. e) The tube functions as gripper to move SiO_2 (diameter: 4.4 mm) sphere away from a hot plate. f) Assembly of different modes of alignment in the same tube. The direction of orientation in left part is longitudinal and the direction of orientation in right part is peripheral. The left part shows reversible 48% elongation and the right part shows reversible expanding. The diameter of expanded part is 5.7 mm and its original diameter is 4 mm. Scale bar: 5 mm. In (a)–(d) and (f), the temperature in left optical photographs is 100 °C and the right is room temperature (≈25 °C).

Such complex motions were because that one side of tubes had larger shape change in length than the other. The top side elongated by about 44% and the bottom side was about 35% when cooling down from the isotropic phase. When the temperature went up ($T > T_i$), both sides of tubes restored the balanced state. In the above LCE tubes, the director of oriented liquid-crystal units has been in accordance with the longitudinal direction of tubes. Tangential alignment can be achieved by irradiating the tube while its diameter is enlarged by enclosing a larger solid pillar inside the tube. The light-induced exchange reaction fixes the alignment along the peripheral direction. When oriented along the peripheral direction, tubular LCEs can function as grippers to capture and move objects away from a hot to cold place (Figure 2e). Compared to reversible change of length due to the longitudinal alignment, reversible contraction and expansion of the tube in the peripheral direction is caused by the tangential alignment (Figure 2f). This tubular LCE gripper is different from traditional grippers. Most reported grippers consist of several tentacles that deform together to grasp objects.[23] The drawback of multiarmed grippers is that if one of tentacles fails, it may sabotage the mission of grasping. When it comes to tubular grippers, they grab the specific object by wrapping it around instead of relying on several tentacles.[24]

Because of flexible control of light, programming different modes of locomotion in different regions of the same tubular LCEs is convenient. For tubular robots to execute specific task, it is vital yet very tricky to enable different parts with different locomotion. For example, to move an object, it should include the following movements: the arm reaches the object first, the hand grasps it, and then the arm retracts to get the object and the hand drops it. As a demonstration of different modes of locomotion in different regions without assembly of different tubes, we processed the tubular actuator of which the left part had reversible elongation in length and the right part had reversible expanding in the peripheral direction (Figure 2f). The right part was processed in the method described above while the left part was shielded with a piece of paper and the left part was processed by irradiating under uniaxial tension while the right part was shielded. With proper stimuli, this tube can be used to move an object as a robot arm.

The tube here can be made photoresponsive to get local on-demand actuation and show omnidirectional bending. For remote control of tubular robots, infrared light is a superior stimulus. It is much safer than UV light and has longer penetration depth. Portable infrared light is also much more accessible than the high-power magnetic field often used in actuation. Furthermore, it offers precise local control. We previously showed the photothermal effect of biocompatible polydopamine enabled a shape-memory film to be responsive to infrared light.[25] In this work, we also use the same method by immersing the tube in dopamine solution. The details of coating process are given in the Supporting Information. After the treatment by PDA surface coating, the aligned tubular actuators were able to respond to infrared light. Once the IR light is on, the irradiated site is heated. According to infrared thermal images of a PDA-coated tube irradiated with light (Figure S9, Supporting Information), the temperature of the irradiated site rose rapidly to 80 °C which was higher than T_i in a few seconds. As a consequence, the irradiated site was isotropic and contracted so that the irradiated side was shorter than the unirradiated side and bending happened in order to accommodate the asymmetric deformation. The tubular actuators exhibited omnidirectional bending. Quick and omnidirectional bending is crucial to improve the dexterity of the tubular robots. Here, omnidirectional bending is achieved by casting infrared light to the desired position of PDA-coated tube (**Figure 3**a, and Video S1 and S2, Supporting

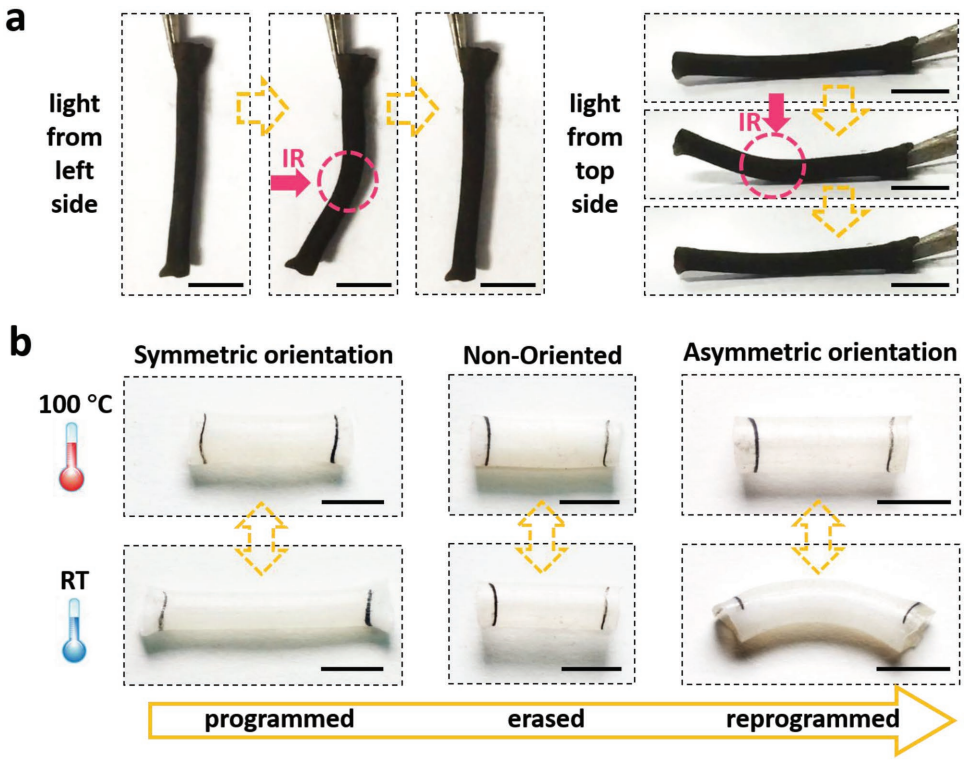

Figure 3. Omnidirectional bending and recycle of a typical tube. a) A straight tube with PDA coating shows omnidirectional bending when infrared light is cast from the left side or top side. b) Erasing the autonomous elongation and reprogramming the tube into bending actuation for a new purpose. Scale bar: 5 mm.

Information). The direction and location of reversible bending depends on where the infrared light is focused on. After turning off the light, the irradiated side was cooled and the mesogens became ordered spontaneously to restore the length which was the same as the length of unirradiated side. By adjusting the light intensity and the exposed location of the tube, the curvature and the position of the bending can be changed.

In spite that the alignment attained is relatively stable, the alignment of the tube and the resultant locomotion can still be erased and reprogrammed. The topological changes of the LCE are based on the exchange reaction of allyl sulfide functional groups. So long as there are radicals, this reaction can be activated. Even though the photoinitiators are consumed during the alignment, new photoinitiators can be introduced again into networks by swelling LCEs in solutions containing photoinitiators. After the evaporation of solvent, the LCEs can be realigned. We first verified the viability of this strategy using LCE films. We found that in the presence of new photoinitiators, the alignment of the film can be erased by UV irradiating when the film was heated to the isotropic state. After the deletion of alignment, the film could be realigned (Figure S10, Supporting Information). Using this strategy, we reprogrammed a tube into different modes of actuation. As shown in Figure 3b, the mode of actuation has been adapted from elongation to bending. Alignment can be erased easily by stress relaxation at the isotropic state induced by external UV-light and regained by tension when networks become adaptable once again. Erasing the existing orientation makes it possible to recycle the aligned actuators.

In summary, we have demonstrated a new strategy to fabricate recyclable untethered tubular soft actuators with complex movements based on a single LCE with allyl sulfide functional groups. The photoinduced topological change allows flexible control of alignment in both the longitudinal and peripheral directions of tubes. As a result, the LCE tubes show complex motions such as reversible simultaneous bending and elongation and simultaneous expansion and elongation, which have not been achieved in the past with any soft tubular actuator or robot. Omnidirectional bending of the tubes with polydopamine coating can be controlled remotely by infrared light. The facile processing method enables the site-specific introduction of different modes of locomotion into one tubular actuator, avoiding the necessity to assemble multiple tubes with different modes together. Moreover, tubes can be reprogrammed for different modes of locomotion while maintaining good stability and solvent resistance. The modes of locomotion demonstrated here are only some examples. Our strategy could be extended to other kinds of motions such as walking, jumping, and so on. According to this strategy, not only straight tubes can be processed, other kinds of geometry can also be fabricated using suitable molds. Furthermore, mechanical properties of the tubes can be adjusted by choosing different monomers in the future to accommodate various applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

dynamic covalent bonds, grippers, liquid crystalline elastomers, soft robots, tubular actuators

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