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Muscle-Mimetic Synergistic Covalent and Supramolecular Polymers: Phototriggered Formation Leads to Mechanical Performance Boost

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ABSTRACT: A thin filament stimulated by Ca²⁺ to combine with myosin is the structural basis to achieve filament sliding and muscle contraction. Though a large variety of artificial materials has been developed by mimicking muscle, the on-demand combination of the actin filament and myosin has never been precisely reproduced in polymeric systems. Herein, we show that both the combination process and the combined structure of actin filament and myosin have been mimicked to construct synergistic covalent and supramolecular polymers (CSPs). Specifically, photoirradiation as a stimulus induces the independently formed covalent polymers (CPs) and supramolecular polymers (SPs) to interact with each other through activated quadruple H-bonding. The resultant CSPs possess a unique network structure which not



only facilitates the synergistic effect of CPs and SPs to afford stiff, strong, yet tough materials but also provides efficient pathways to dissipate energy with the damping capacity of the representative material being higher than 95%. Furthermore, muscle functions, for example, by becoming stiff during contraction and self-growth by training, are imitated well in our system via *in situ* phototriggered formation of CSP in the solid state. We hope that the fundamental understanding gained from this work will promote the development of synergistic CSP systems with emergent functions and applications by mimicking the principle of muscle movements.

INTRODUCTION

Supramolecular polymers (SPs) have been recognized as crucial components for living systems due to their roles in biological functions, such as cell division, mediator for actuation, and regulation of physiological process.^{1,2} In fact, for many of these biological functions, their implementations not only rely on individual supramolecular polymers but also need the cooperation of specific covalent polymers (CPs). The working mode of myofibril in muscle contraction is a typical representative according to the sliding filament theory.³⁻⁶ Actin filament, a kind of SP in thin filament formed by supramolecular assembly of actin, possesses a large number of binding sites in its structure. When it receives the stimulus of Ca²⁺, the blocked binding sites are exposed and then bind to the head of myosin (CP in thick myofilament) through supramolecular interactions (Figure 1a). The stimulustriggered noncovalent combination of actin filament and myosin is the structural basis to achieve the filament sliding. Such a polymeric system with CPs and SPs working synergistically can be called synergistic covalent and supramolecular polymers (CSPs).⁷ Inspiration is often drawn from nature to solve problems existing in artificial materials.^{8,9} Generally, individual CPs or SPs have their own advantages but also possess inherent limitations for practical applications.^{10–19} The powerful functions of myofibril indicate that the elegant combination of CPs and SPs through proper interactions is a promising strategy to produce advanced materials. Nevertheless, the complicated structures of CPs and SPs as well as their on-demand combination in myofibril show that developing artificial synergistic CSPs by mimicking myofibril for specific properties or functions is a significant challenge.

The construction of artificial synergistic CSPs needs to rationally integrate SPs and CPs in one system. In 2016, Stupp et al. designed an ingenious system in which covalent and noncovalent polymerizations took place simultaneously to form hybrid polymers as cylindrical fibers, and noncovalent polymerization.²⁰ Whereafter, the same group further created hybrid systems with fascinating actuation properties by adopting sequential supramolecular and covalent polymerizations.^{21,22}

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Article



Figure 1. Design of muscle-mimetic synergistic CSPs. (a) Actin filament, myosin, and their combination triggered by Ca^{2+} in myofibril, which act as the inspiration source. (b) Schematic representation and chemical structures of the CPs, SPs, and the photoinduced formation of synergistic CSPs to mimic myofibril.

Almost simultaneously, our group utilized the successive covalent and supramolecular polymerizations to obtain synergistic CSPs, which exhibited peculiar robust yet dynamic properties.⁷ These simultaneous and sequential strategies stand for a significant advancement toward constructing synergistic CSPs. However, synergistic CSPs similar to myofibril, in which CPs and SPs are independently formed and then connected on demand to function by stimulus-triggered supramolecular interactions, have yet to be achieved.

Herein, we report a de novo chemical design of the synergistic CSP system in which both the responsive combination and corresponding covalent and supramolecular structures of the myosin and actin filament during muscle contraction are reproduced. Specifically, similar to the Ca²⁺induced combination of actin filament and myosin, photoirradiation as a stimulus was employed to induce the independent CPs and SPs to interact with each other through activated quadruple H-bonding, thereby leading to the formation of synergistic CSPs in a new way. The representative synergistic CSP exhibits good mechanical properties, including the aspects of stiffness (Young's modulus = 145 MPa), strength (maximum stress = 12.0 MPa), ductility (1506%), and toughness (136 MJ/m³). Particularly, it also has unusual performance in energy dissipation with a damping capacity higher than 95%, which implies its enormous potential as mechanically adaptive materials. These superior performances benefit from the delicate muscle-mimetic structure, that is, a tough but dynamic network formed by supramolecular interactions connected CPs and SPs. Furthermore, the photoinduced *in situ* combination of CPs and SPs in the solid state endows the material with muscle-like functions. Upon irradiation, the material becomes stiff like muscle behaving during a contraction. Besides, the photostimulus also gives rise to simultaneous enhancement of self-healing efficiency and mechanical strength of the CSP, which is reminiscent of muscle growth based on the reconstruction of fibril after physical exercise.

RESULTS AND DISCUSSION

Design, Synthesis, and Structural Characterization. To achieve the goal of mimicking myofibrils, the two components of CPs and SPs first need to be rationally designed. As shown in Figure 1b, the CPs adopted here are polynorbornene derivatives prepared by ring-opening metathesis polymerization (ROMP). The side chain of the CPs decorates with a large number of 2,7-diamido-1,8-naphthyridine (DAN) units, which is designed to imitate the structure of thick myofilaments possessing many myosin heads arranged on their surface (Figure 1a). The SPs mimicking the thin filaments rely on a special monomer with three functional

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Figure 2. Partial ¹H NMR spectra (400 MHz, CDCl₃, 298 K) of pure SP (a) and SP mixed with CP-2 followed by UV irradiation (b). AFM phase images of CSP-2 (c) and control-2 (d).

groups (Figure 1b). The group of benzo-21-crown-7 (B21C7) and its complementary secondary ammonium salt are able to bind with each other through host-guest recognition to form the SPs (Figure 1b). The remaining functional group, namely, the 2-ureido-4[1H]-pyrimidinone (UPy) moiety, serves as the binding site like that on the thin filament which is initially protected by nitrobenzyl group. In myofibril, the Ca2+ stimulates the thin filament to uncover the binding sites for myosin, hence realizing the combination of actin filament and myosin. Such a biological process is readily reproduced in this work. When the UPy binding sites are protected by nitrobenzyl groups, the combination between the CPs and SPs is prohibited. However, once stimulated by UV irradiation, the UPy sites can be deprotected and exposed. It has been found that the UPy unit is able to selectively form strong heterocomplementary quadruple H-bonds with the DAN group.²³⁻²⁵ Therefore, the photoirradiation leads to the integration of independent CPs and SPs to form synergistic CSPs connected by activated quadruple H-bonding. Different from the simultaneous or sequential covalent and supramolecular polymerizations, by mimicking myofibril, we employ a fully new method of stimulus-induced combination (SIC) to afford synergistic CSPs.

The density of the DAN units on the CPs can be tuned by controlling the ratio of the dilute monomer, that is, norbornenyl *exo*-di-*n*-butyl ester. In this way, three CPs with different DAN contents were prepared. By mixing these three CPs with SPs in a 1:1 molar ratio of DAN and UPy moieties followed by photoirradiation, we constructed synergistic CSP-1, -2, and -3 (Figure 1b). To deeply understand the properties of the CSPs, two control samples corresponding to CSP-2 were also designed (Scheme S2). In the structure of control-1, the amino group is not in the form of secondary ammonium salt, but protected by the Boc group, which hampers the host–guest recognition to form SPs. The control-2 is a sample whose DAN units are acidized by HPF₆ to destroy the possible weak H-bonding. As such, the CPs and SPs in control-2 are simply mixed.

The syntheses of the key monomers, CPs, and SP are summarized in the Supporting Information. The CSP-2 was prepared by photoirradiation of the mixed CP-2 and SP in solution ($\lambda = 365$ nm). As exhibited in the ¹H NMR spectra (Figure 2b), the characteristic NH protons of the UPy moiety were obviously different from those on the UPy-UPy dimer formed by irradiation of pure SPs (Figure 2a), but highly consistent with the formation of UPy-DAN heterodimer.^{23–26} Therefore, the mixed CP-2 and SP in solution interacted with each other through heterocomplementary quadruple H-bonding to form CSP-2 upon photoirradiation. Particularly, the integrated structure of the CSP-2 was well preserved in the

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Figure 3. (a) DSC curves of CSP-1, -2, and -3 and control-1 and -2 recorded by the second heating scan from -40 to 90 °C with a heating rate of 20 °C/min. (b) Stress-strain curves of CSP-1, -2, and -3 recorded with a deformation rate of 100 mm/min. (c) Young's moduli and toughness of CSP-1, -2, and -3 calculated based on their stress-strain curves. (d) Stress-strain curves of CSP-2 and control-1 and -2 recorded with a deformation rate of 100 mm/min. (e) Young's moduli and toughness of CSP-2 and control-1 and -2 recorded with a deformation rate of 100 mm/min. (e) Young's moduli and toughness of CSP-2 and control-1 and -2 calculated based on their stress-strain curves. (f) Ashby plot of "toughness" and "strain at break" of CSP-2 and other reported polymer systems classified into CSPs in literatures.

bulk state, which was proved by the solid-state ¹³C NMR (Figure S36). Besides, the morphology study by atomic force microscopy (AFM) also supported the combination of CPs and SPs. For example, compared with the phase image of CSP-2 (Figure 2c), more distinct phase separation was observed in the image of control-2 whose CPs and SPs cannot interact with each other (Figure 2d). It is reasonable that the formation of heterocomplementary quadruple H-bonding are beneficial to the blend of CPs and SPs to inhibit their self-aggregation. In addition, the lower phase shift of CSP-2 than that of control-2 indicates higher elasticity of CSP-2, which also supports the strong interaction of the CPs and SPs in CSP-2.

Thermal Properties of the CSPs and Controls. Thermal gravimetric analysis (TGA) study showed that all samples including CSP-1, -2, and -3 and control-1 and -2 had good thermal stability with the decomposition temperatures higher than 200 °C (Figure S38). The differential scanning calorimetry (DSC) of the samples were also studied (Figure 3a). The glass transition temperature (T_{o}) values of CSP-1, -2, and -3 were measured as 64, 33, and 8.0 °C, respectively, showing a decreasing tendency. It can be explained that the quadrupole H-bonding-modulated CPs and SPs are able to form a network structure, and the networks with more UPy-DAN connection points generally restrict the motion of the chain segments more powerfully, thus exhibiting higher T_{g} . In addition, due to the lack of interchain interactions, the T_{σ} values of control-1 (1.0 °C) and -2 (29 °C) were lower than that of CSP-2.

Fundamental Mechanical Properties of the CSPs and Controls. In myofibril, the combination of actin filament and myosin offers a strong structure to support the filament's sliding. To explore whether their typical mechanical properties are able to emerge in our artificial system, a series of tensile tests were performed. The stress-strain curves of CSP-1, -2, and -3 were shown in Figure 3b. Young's moduli of the samples increased with the density of connection points and the values are 156, 145, and 39.7 MPa for CSP-1, -2, and -3, respectively (Figure 3c). The strain at break had the opposite trend with the values of 15% for CSP-1, 1506% for CSP-2, and 2465% for CSP-3 (Figure 3b). Except for CSP-1 with a brittle-hard property, both CSP-2 and -3 had outstanding performance in toughness with the values of 136 and 122 MJ/m³, respectively (Figure 3c). Among these three samples, the CSP-2 has more balanced properties, which might be due to its appropriate density of connection points, and thus would be focused on in the following sections.

Subsequently, the mechanical properties of CSP-2 were compared with those of the two control samples. There was no obvious advantage of CSP-2 in terms of ductility due to the character of linear polymer for control-1 and -2 (Figure 3d). However, it was much more superior for CSP-2 in other mechanical properties. The Young's moduli were 145 MPa for CSP-2, 0.6 MPa for control-1, and 34.5 MPa for control-2, and the maximum stresses for the three samples were 12.0, 0.2, and 3.1 MPa, respectively (Figure 3e). Such an obvious advantage was also observed in the aspect of toughness which showed the values of 136 MJ/m³ for CSP-2, 10.8 MJ/m³ for control-1, and 28.2 MJ/m^3 for control-2 (Figure 3e). As for the two controls, control-1 can be regarded as a linear CP, and control-2 possesses coexisting CPs and SPs. However, there is no significant interaction between them. Therefore, the prominent properties of CSP-2 originate from the synergistic effect of CPs and SPs, which is closely related to the photoactivated quadruple H-bonding connection points. Notably, the mechanical properties of the CSP-2 are also compared with the reported cases which are classified as synergistic CSPs according to the principle of which supramolecular interactions in polymer structures could connect with each other to form distinct SP chains.²⁷⁻³⁵ As shown in Figure 3f, in terms of strain at break and toughness, our CSP-2 is superior to the others, which might be due to the unique muscle-mimetic structural design of our system.



Figure 4. (a) Cyclic tensile test curves of CSP-2 and control-1 and -2 at a strain of 500% under the deformation rate of 100 mm/min. (b) Energy dissipation and damping capacity of CSP-2 and control-1 and -2 calculated based on the loading/unloading curves. (c) Cyclic tensile test curves of CSP-2 recorded with increased maximum strains. (d) Energy dissipation and damping capacity for each circle of the cyclic tensile test curves.



Figure 5. (a) Cyclic temperature ramp curves of CSP-2 in the range of 40-80 °C with a heating/cooling rate of 5.0 °C/min. (b) Stress relaxation experiments of CSP-2 at different temperatures. (c) Strain sweep rheological analysis of CSP-2 at a constant angular frequency of 1.0 rad/s. (d) Master curves of CSP-2 at a reference temperature of 40 °C. (e) Tensile stress-strain curves of CSP-2 at different stretching rates. (f) Fitting curve of yielding stress as a function of logarithm of strain rate.

Energy Dissipation of the CSPs and Control Samples. In addition to the highlighted fundamental mechanical properties, the synergistic CSPs also have unusual performance in energy dissipation. Energy dissipation reflects the ability of the materials to convert the mechanical energy into heat, which can be calculated by integrating the area of the cyclic tensile curves. As shown in Figure 4a, with the same strain of 500%, the area of CSP-2 was much larger than those of the two control samples, and the values of the energy dissipation were calculated as 34.9 MJ/m³ for CSP-2, 0.80 MJ/m³ for control-1, and 9.30 MJ/m³ for control-2. Damping capacity, which is defined as the ratio of energy dissipation to the incoming energy,^{36,37} was calculated as 95.1, 65.8, and 89.6% for CSP-2 and control-1 and -2, respectively (Figure 4b). One of the most prominent features of these results was that the damping capacity of control-1 is much weaker than those of the other samples. On the basis of their structural differences, it is reasonable to speculate that the SPs play a vital role in energy dissipation. In addition, the damping ability of CSP-2 was superior to that of control-2 where CPs and SPs do not have significant interactions and higher than the reported CSP with the CPs and SPs connected by a covalent bond in our previous work (86.5%).⁷ These observations suggest that the good damping capacity of CSP-2 originates from its unique structure, where the CPs and SPs are connected by quadruple H-bonding. This speculation is further supported by the high damping capacity of CSP-3 (91.2%).

The progressive loading-unloading experiments of CSP-2 were conducted to trace the changes of energy dissipation and damping capacity on different strains (Figure 4c,d). The energy dissipation increased almost linearly with the applied strains of the sample, and the value of energy dissipation at an applied strain of 1400% reached 125 MJ/m³, indicative of good energy dissipation ability. Different from energy dissipation, the damping capacity of CSP-2 always maintained at a high level in the strain range of 100-1400%, and the mean value under all strains was 95.6%. Therefore, the damping capacity of CSP-2 was relatively stable and independent of varied deformations. The comparison of damping capacity between CSP-2 and different kinds of the reported energy dissipating materials were summarized in Figure S42. It was found that the damping capacity of CSP-2 is higher than most of the energydissipation materials including bulky polymers,^{38,39} hydro-gels,^{40,41} and natural materials^{42,43} and is comparable to the hydrogel fibers which set the record in damping capacity.³ These results mean that the muscle-mimetic design would make our CSP-2 a good candidate for energy absorption applications.

Insights into the Structure–Property Relationship of CSP-2. The above studies have disclosed that the CSP-2 possesses good mechanical properties and damping ability, which results from its peculiar biomemetic structure. Then, to figure out the relationships between the properties of the CSP-2 and its structure, a series of rheology measurements were carried out. The results of cyclic temperature ramp of CSP-2 were shown in Figure 5a. When the temperature was ramped up from 40 to 80 °C, both the G' and G'' substantially decreased, and a peak emerged around 59 $^{\circ}$ C in the tan δ curve at the same time, indicating the existence of a transition. An opposite viscoelastic transition was observed in the ramp-down process. Intriguingly, the two tan δ curves overlapped well with each other above 57 °C but showed an evident hysteresis below that temperature. The reason for this phenomenon might be that 57 °C can be seen as a critical temperature, that is, above it the supramolecular interactions start to dissociate, but their reassociation at lower temperature has a time delay, thus leading to the hysteresis.

The stress relaxation experiment is an effective tool to reveal the structure information on polymers from their mechanical behaviors. Obvious relaxation could be observed in all stress relaxation curves recorded at different temperatures, but the relaxation rate increased at elevated temperatures (Figure 5b). The extent of the stress relaxation was also highly dependent on the temperature: Similar to the polymers with permanent cross-links, the applied force was kept at lower temperatures $(30-50 \ ^{\circ}C)$ even extending the relaxation time to 1 h, but it could be quickly and fully released at temperatures higher than 60 °C, like the behavior of linear polymers. These results support that synergistic CSP-2 has a network structure. At temperatures lower than 50 °C, the topological structure is frozen by the network, leading to the slow and incomplete stress relaxation. In contrast, stress relaxation is accelerated when the network structure is fractured by temperatures higher than 60 °C. Besides, the network started to break at 60 °C is consistent with the result of the temperature ramp test. These analyses were further supported by the strain sweep tests (Figure 5c). At a lower temperature (35 °C), a narrow linear

viscoelastic region (about 2%) was observed because the network was intact at this temperature, and the increase of strain was accompanied by the damage of the network structure through the dissociation of supramolecular interactions. In contrast, the network decomposed at 70 °C; thus, corresponding curves exhibited broad linear viscoelastic region (~100%). It could be speculated that the stress relaxation may mainly result from the decomposition of network arising from the dissociation of host–guest recognition, but weakening and/or even dissociation of the quadruple H-bonding at high temperature should also contribute to it.

To comprehensively demonstrate the dynamic behaviors of the CSP at different time scales, the master curves were obtained at the reference temperature of 40 $\,^{\circ}\text{C}$ for CSP-2 by using the time-temperature superposition (TTS) principle (Figure 5d). The high-frequency region (>10⁻² rad/s) with G'> G'' was the glassy regime where the network was frozen. Below the crossover point of 10^{-2} rad/s, the region was assigned as the dissipative regime (G' < G''). The superimposed curves in this regime were recorded at temperatures higher than 60 °C which could weaken or dissociate the supramolecular interactions of host-guest recognition and quadruple H-bonding as analyzed above, thus resulting in dissipative behaviors. Notably, partial restriction of dynamics was observed in the range of $10^{-8}-10^{-5}$ rad/s. Since the supramolecular interactions should be basically in an uncomplexed state at such lower frequencies (corresponding to high temperatures), the observation might be related to Rouse dynamics of the CP chains. The terminal regime of the curves, lower than 10^{-8} rad/s, was the viscous flow regime. The slope values lower than the true terminal relaxation, that is, G' and G'', are 2 and 1, respectively, were an indication of secondary interactions affecting the chain dynamics.^{44,45} In addition, the superposition of the data failed starting from 60 °C to higher temperatures, which was consistent with the structure changes of the CSP-2. It is noteworthy that the regime of the elastic plateau was absent in the curves, but it was commonly observed in the system with strong network structures including covalent bond connected CSPs in our previous work.⁷ The phenomenon implies that the CSP-2 has a highly dynamic network structure.

Moreover, to evaluate the energy required for initially fracturing the network, tensile tests with different stretching rates were performed and showed that the mechanical properties of CSP-2 were highly stretching-rate-dependent (Figure 5e). The plot of yielding stress against the logarithm of deformation rate in Figure 5f had a linear relationship in accord with the Eyring model of the mechanically induced dissociation of noncovalent bonds:^{46,47}

$$\dot{\epsilon} \approx e^{-(E_y - 0.5\sigma_y V_a)/(k_b T)}$$

 $\dot{\varepsilon}$, σ_y , E_{yy} and V_a are the strain rate, yielding stress, activation energy, and effective activation volume, respectively. The activation volume extracted by data fitting was 5.8 nm³, which can be regarded as the size of polymer segments involved in the motion associated with yielding. The apparent activation energy used to evaluate the energy barrier to overcome the mobile segments was calculated to be 23.0 kJ/mol. For CSP-2, the initial fracture of the network structure might be responsible for the yielding; hence, the energy to destroy the intact network through the dissociation of supramolecular interactions is about 23.0 kJ/mol.

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Figure 6. (a) Photographs of the film before and after irradiation. (b) Force separation curves of the film before and after irradiation from the retraction of the cantilever. (c) Young's moduli extracted from the force separation curves of the film before and after irradiation. (d) Storage modulus as a function of irradiation time for CSP-2. (e) Stress-strain curves of CSP-2 recorded with a deformation rate of 100 mm/min. (f) Stress-strain curves of the virgin and healed CSP-2 specimens with and without irradiation recorded with a deformation rate of 100 mm/min. (g) Young's moduli and maximum stress calculated based on the stress-strain curves of the healed CSP-2 specimens with and without irradiation.

Assisted by the working mechanism of the myofibril, the structure-property relationships of our CSPs can be established. In myofibril, the combination mode of actin filament and myosin plays a crucial role in filament sliding. On the one hand, the binding force, namely, supramolecular interaction, is strong enough to support the sliding of actin filament driven by the myosin; On the other hand, the combination is also dynamic, such that the combined actin filament and myosin are easily to be separated after accomplishing one cycle of filament sliding. Such a critical role of supramolecular connections is also reflected in our CSP systems. The activated quadruple H-bonding, as cross-links of the CPs and SPs, could facilitate the two components to work synergistically, thus leading to the stiff yet tough material. Moreover, apart from the quadruple H-bonding connections, the SPs are formed by host-guest recognition, both of which make our CSPs a highly dynamic network. When external stress is applied to the CSPs, the network is readily to dissipate energy through various pathways, eventually showing unusual behavior in energy dissipation. Therefore, the unique musclemimetic structure in which the CPs and SPs are cross-linked by supramolecular interaction endows the materials with prominent mechanically adaptive properties.

Muscle-Mimetic Functions of CSP-2. As mentioned above, on the basis of the combination of CPs and SPs, the filament sliding gives rise to the muscle contraction, and becoming stiff is one of the most obvious characteristics during the process. In addition, the strength of muscles could be enhanced by training in which the destruction and reconstruction of the fibril lead to the growth of muscles.⁴⁸⁻⁵⁰ Both functions of muscles involve complicated dynamic processes and thus are difficult to mimic in the fabrication of artificial materials. Given the good mechanical performance and unique dynamics of CPs and SPs is possible in the

solid state, then these two muscle functions would be achieved in a sense in our artificial system.

In order to verify the possibility, films containing independent CPs and SPs with protected UPy were first made. After 2 h of irradiation, an obvious color change was observed from an initial dark yellow to a final brown (Figure 6a), which was attributed to the deprotection. Modulus measurements of the films before and after irradiation were performed using AFM, and the corresponding forceseparation curves were shown in Figure 6b. It is well-known that the slope of the retract curves is linearly related to the stiffness of the materials. Hence, the higher slope of the curve after irradiation demonstrated that the film became much stiffer. The Young's moduli extracted from the retract curves were 3.40 and 104.3 MPa for the samples before and after irradiation, respectively (Figure 6c). On the basis of these results, it is reasonable to conclude that the photoinduced combination of CPs and SPs could stiffen our CSP material in the solid state, reminiscent of the Ca²⁺-triggered muscle contraction.

The changes of mechanical properties during the photoinduced integration could be traced in situ by the rheometer equipped with a light-emitting diode (LED) fixture. The resulted plot of the storage modulus against irradiation time were shown in Figure 6d. Before irradiation, the storage modulus was constant. When the irradiation started at the time of 2 h, the modulus increased gradually with the irradiation time, and it tended to level off after being irradiated for 3 h. This result implied that the materials with various stiffness can be obtained by controlling the irradiation time, which is meaningful for various applications. Subsequently, the mechanical property changes of the irradiated film were further characterized by macroscopic tensile tests, which showed a distinct enhancement compared with sample before irradiation (Figures 6e and S48). Before irradiation, the values of Young's modulus, maximum stress, and toughness for the

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system were 26.0 MPa, 3.20 MPa, and 20.6 MJ/m^3 , respectively. In contrast, these parameters were enhanced to 84.6 MPa, 10.6 MPa, and 66.2 MJ/m^3 after irradiation. Therefore, these results indicate that the photoinduced combination of CPs and SPs could enhance the mechanical properties of the materials, and such a phenomenon is somewhat similar to the function of stiffness change shown by muscle contraction.

Structural reconstruction after damage along with enhanced mechanical properties are the main features of self-growing materials. Here, photoinduced self-healing of our material was investigated. As shown by the stress-strain curves (Figure 6f), the sample without irradiation was only restored a little, as shown by the limited breaking strain of 14.3% after 2 h of healing. In contrast, the sample with 2 h of irradiation could be stretched up to 121% of its original length. Furthermore, the overall mechanical properties of the material were also improved upon irradiation. As shown in Figure 6g, the Young's modulus was enhanced from 26.0 to 78.8 MPa, and the maximum stress was improved from 3.60 to 10.3 MPa. As such, the self-healing process is accompanied by marked mechanical property enhancement, resembling the self-growing behavior of muscles after physical exercise.

CONCLUSIONS

In summary, inspired by the working mechanism of myofibril during muscle contraction, we have designed a polymeric system in which the combination of CPs and SPs was triggered by photoirradiation to generate synergistic CSPs cross-linked by activated quadruple H-bonding. Both the combination process and the resultant covalent and supramolecular structures in CSPs are similar to those of actin filament and myosin in myofibril. The results of tensile tests exhibited that the synergistic CSPs had remarkable mechanical properties in terms of stiffness (Young's modulus = 145 MPa), strength (maximum stress = 12.0 MPa), ductility (1506%), and toughness (136 MJ/m³). Furthermore, they also possessed unusual ability in energy dissipation with the damping capacity above 95% in a large strain range of 100-1400%. Rheology measurements revealed that the tough but dynamic network structure, constructed by mimicking myofibril, is responsible for the good mechanical performance. Particularly, the material with photoinduced combination of CPs and SPs in the solid state exhibited muscle-like functions. The stiffness change observed in muscle contraction was reproduced in our artificial materials whose strength was obviously enhanced upon irradiation. The training-induced growth of muscle was also mimicked by our material in which photoinduced self-healing and enhancement of mechanical properties took place simultaneously. The muscle-mimetic design with a phototriggered structure and property modulation of our CSPs could find broad potential applications as smart supramolecular materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c10918.

Experimental details and additional data (PDF)

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Notes

The authors declare no competing financial interest.

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