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Toughening a Self-Healable Supramolecular Polymer by Ionic Cluster-Enhanced Iron-Carboxylate Complexes

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Abstract: Supramolecular polymers that can heal themselves automatically usually exhibit weakness in mechanical toughness and stretchability. Here we exploit a toughening strategy for a dynamic dry supramolecular network by introducing ionic cluster-enhanced iron-carboxylate complexes. The resulting dry supramolecular network simultaneously exhibits tough mechanical strength, high stretchability, self-healing ability, and processability at room temperature. The excellent performance of these distinct supramolecular polymers is attributed to the hierarchical existence of four types of dynamic combinations in the high-density dry network, including dynamic covalent disulfide bonds, noncovalent H-bonds, iron-carboxylate complexes and ionic clustering interactions. The extremely facile preparation method of this self-healing polymer offers prospects for high-performance low-cost material among others for coatings and wearable devices.

Polymers that undergo autonomous healing are mimicking intrinsic properties of biosystems and are highly desirable for many applications because they can endow materials with the capability to repair mechanical damage.^[1] To realize self-healing properties, some strategies have been developed, especially using dynamic reversible noncovalent transformations to induce the reformation of damaged interfaces.^[2–7] Taking advantage of the supramolecular toolbox that is, H-bonds,^[2] host–guest combinations,^[3] metal–ligand interactions,^[4] ionic bonds,^[5] dynamic covalent bonds,^[6] dipole–dipole interactions,^[7] and even van der Waals force,^[1c] have shown to be versatile features in the design of self-healing gels and polymers. However, there remain some very challenging issues facing the design of a self-healing supramolecular network: i) The introduction of weak but reversible noncovalent bonds into the network usually decreases significantly the stiffness of the network, leading to a self-healing but soft network; ii) The introduction of noncovalent bonds, especially based on hierarchical multi-component systems

often requires complex synthetic procedures increasing material costs; iii) Many self-healing polymers contain or involve external solvents to support the supramolecular recognition processes, while developing self-healable dry polymers is more preferable for industrial application.^[1,2,8]

Very recently, our lab developed an unprecedented supramolecular polymer using the natural small molecule,^[8] thioctic acid (TA), as the main feedstock. A crosslinked solid polymer was obtained by a facile co-mixing method of molten TA liquid, 1,3-diisopropenylbenzene (DIB) and minimal FeCl₃, involving no external solvent. The crosslinked supramolecular network is capable to function as a self-healable elastomer at ambient temperatures. However, the resulting materials exhibit very low mechanical moduli of less than 90 kPa, limiting the further applications in high-strength self-healable materials. The weakness in mechanical moduli mainly rested on the discrete distribution of iron-carboxylate complexes and demanded for a toughening strategy applicable to a dynamic self-healing system. We anticipated that the secondary clustering interactions of these ionic complexes could possibly strengthen the dynamic supramolecular network by high-affinity Coulombic force, especially to be expected in a solvent-free dry network.

Herein, we demonstrate that a dry supramolecular network can be remarkably toughened by abundant iron-ion crosslinking (1% molar ratio of monomer TA) (Figure 1), enhancing the mechanical moduli of the polymers over 60 times, meanwhile maintaining the high stretchability and self-healing capability of the dynamic network. The ionic cluster effect of iron-carboxylate complexes is found to be a secondary crosslinking interaction in this solvent-free network. Significantly, three commercial feedstocks and a little heat are all that's needed to make such high-performance supramolecular polymers that simultaneously integrate high toughness, high stretchability, self-healing ability, processability, and recyclability. We envision that this developed dynamic network offers opportunities towards applications in low-cost high-performance self-healing materials.

The preparation of poly(TA-DIB-Fe) copolymers with high iron(III)-to-TA molar ratio (1/1000 to 1/50) was based on a modification of our previous procedure.^[8] Specifically, a higher heating temperature (150 °C) was used to decrease the viscosity of the liquid mixture, and the reaction mixture was sealed to protect the system from humidity in air in view of the hydrophilic nature of abundant iron-carboxylate ionic clusters (Figure S1). Upon cooling the molten mixture of TA, DIB, and FeCl₃ to room temperature yellow to brown polymer solids are obtained. Increasing the iron(III) concentration, the sample with an iron(III)-to-TA molar ratio (1/100) turned brown, revealing the formation of ionic clusters

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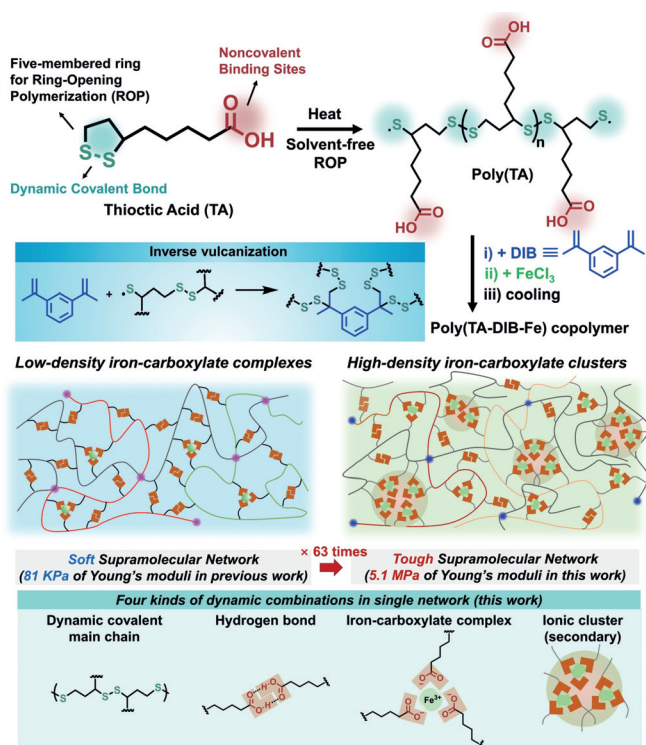


Figure 1. Schematic representation of the TA monomer and poly(TA) polymers. The cartoon representation shows the existed four types of dynamic combinations in the network.

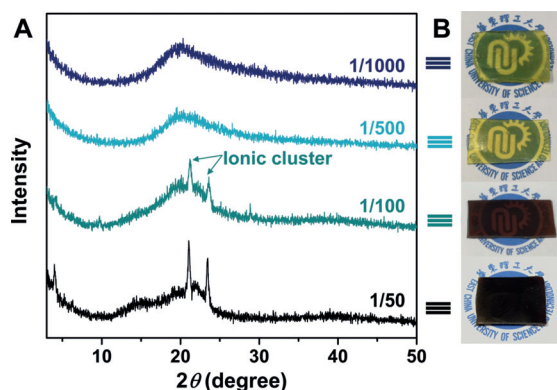


Figure 2. A) XRD patterns and B) photographs of the poly(TA-DIB-Fe) films [iron(III)-to-TA molar ratio of 1/1000, 1/500, 1/100, and 1/50].

due to the typical ligand-to-metal charge transfer.^[9] The polymer film exhibited translucency (Figure 2), which suggested the homogeneous nature of the resulting network.

To further investigate the high-density iron-carboxylate clusters in the material, X-ray diffraction (XRD) was performed, showing the absence of iron oxide species. The observed broad peaks at around 20° indicated the amorphous nature of the poly(TA-DIB-Fe) copolymer network with the iron(III)-to-TA molar ratio lower than 1/500 (Figure 2A) in accordance with our previous study.^[8] However, notable sharp diffraction peaks at 21.2° and 23.6° were observed in the sample with an iron(III)-to-TA molar ratio of 1/100 and 1/50

(Figure 2A), pointing to the formation of metal ionic clusters by Coulombic force among the iron-carboxylate complexes.^[10] Recent literature shows that ionic cluster formation of iron(III)-ligand complexes in a dry polymer network can result in nanosized internal order.^[11] To get further information of the ionic clusters, synchrotron radiation small-angle X-ray scattering (SAXS) was employed (Figure S2 and S3). As a result, all of the poly(TA-DIB-Fe) samples showed no sharp peaks at the tested region, indicating the disordered distribution of the iron-carboxylate clusters in the network. Moreover, grazing-incidence wide-angle X-ray scattering (GIWAXS) further confirmed the amorphous nature of the network by the absence of scattering signals at wide angles (Figure S4). Therefore, the high-density iron(III)-carboxylate complexes in the dry network existed as disordered ionic clusters.

Polymer materials containing ionic bonds usually exhibit humidity-responsive properties.^[12] The water in the air could enter into the network and hydrate the ionic bonds, resulting in the remarkable decrease in mechanical strength,^[12a] which might become a disadvantage in practical applications. Surprisingly, the poly(TA-DIB-Fe) copolymers crosslinked by high-density ionic clusters exhibited excellent humidity-resistance ability, while a reference sample without DIB would be gradually softened and become out-of-shape in the air (Figure S5). The disappearance of ionic cluster signals in the XRD patterns also indicated the hydration-induced dissociation of the iron(III)-carboxylate ionic clusters in the poly(TA-Fe) network (Figure S6). The infrared spectra indicated a low content of hydrated water in the DIB-crosslinked network (Figure S7). The ionic-cluster-toughened network was more stable to humidity and insoluble in water in the presence of DIB (Figure S8 and S9), which should be attributed to the shielding effect of the highly hydrophobic DIB units.

Broadband dielectric spectroscopy (BDS) of the resulting poly(TA-DIB-Fe) copolymers with varied iron(III)-to-TA molar ratios (1/50, 1/100, 1/500, 1/1000) revealed the consistent frequency-dependent conductivity and surface resistance expected for insulator materials (Figure S10).^[13] The variation of the amount of iron(III) ions resulted in slight differences of the dielectric properties of the poly(TA-DIB-Fe) copolymers. However, the hydration of the poly(TA-Fe) sample without DIB led to the remarkable increases in dielectric constant, dielectric loss, and conductivity (Figure S10), which was attributed to the absorbed water molecules and enhanced mobility of the polymer chains.^[14]

Combining the observed results of XRD, SAXS, GIWAXS, and BDS, it can be concluded that the high-density iron(III)-carboxylate complexes existed as ionic clusters in the dry network of poly(TA-DIB-Fe) copolymer. This observation led us to the further exploration of how these ionic clusters affected the mechanical properties of the poly(TA-DIB-Fe) copolymers. The temperature sweeping rheological curves indicated enhanced mobility of the polymer chain with increasing temperature, supporting the noncovalently cross-linked nature of the network (Figure S11). With the increasing iron(III)-to-TA molar ratio ranging from 1/18000 to 1/50, the maximal tension strength increased from 0.05 MPa to

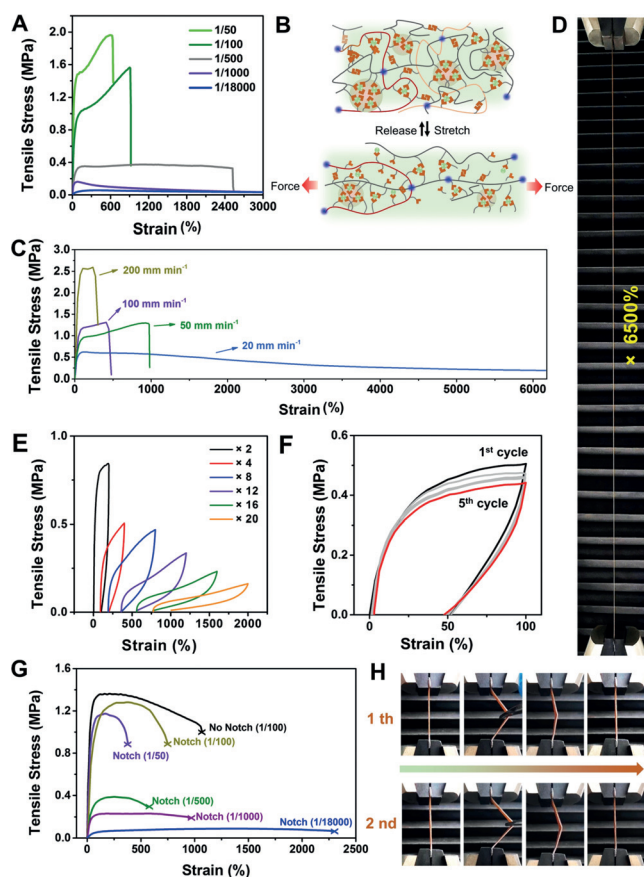


Figure 3. A) Stress–strain curves of the copolymer with different iron(III) concentrations at a loading rate of 50 mm min^{-1} [iron(III)-to-TA molar ratio of 1/50, 1/100, 1/500, 1/1000 and 1/18000, respectively]. B) Energy dissipation mechanism for high toughness and stretchability. C) Stress–strain curves of the copolymer at varied strain rates. D) Photograph of the stretched polymer with an elongation of 6500%. E) Sequential loading-unloading stress–strain curves with no resting intervals at a loading rate of 50 mm min^{-1} . F) Five loading-unloading cycles of the copolymer with 5 min rest intervals at a loading rate of 20 mm min^{-1} . G) Stress–strain curves of the 1/2 notched copolymer films with varied iron contents at a loading rate of 50 mm min^{-1} . The tensile stress of the notched samples has been corrected by the real area after notching. H) Photographs showing the excellent elasticity. Except if indicated, the iron(III)-to-TA molar ratio of tested samples was 1/100.

1.87 MPa, while the Young's modulus increased from $0.086 \pm 0.01 \text{ MPa}$ to $7.78 \pm 0.46 \text{ MPa}$ (Figure 3 A and Table S1). This large enhancement showed the remarkably toughened mechanical performance of the network after crosslinking by high-density iron(III)-carboxylate clusters. The toughening mechanism was attributed to the secondary high-affinity ionic bonding of the iron(III)-carboxylate complexes (Figure 3 B).^[12a, 15] The toughened poly(TA-DIB-Fe) network with an iron(III)-to-TA molar ratio of 1/100 exhibited typical rate-dependent tensile curves (Figure 3 C), in which the sample can be stretched to over 6500% of original length (Figure 3 D) at a lower strain rate of 20 mm min^{-1} . The stretched sample could be also recovered partially (Figure S12). The high stretchability of the toughened polymer might be attributed to the hierarchical operation of four types of

dynamic combinations which work as sacrificial bonds upon stretching (Figure 3 B).

The resulting poly(TA-DIB-Fe) network with an iron(III)-to-TA molar ratio of 1/100 also showed good elasticity. The sample can undergo a complex tension-relaxation process without breaking despite the absence of resting time (Figure 3 E). The cyclic experiments also showed the successful recovery of elastic modulus and high Young's modulus with 5 min test intervals (Figure 3 F). A shorter resting time of 10 s leads to an incomplete recovery of the stretched polymer (Figure S13). These results suggest a sliding mechanism based on dynamic chemical bonds, which required time to realize the strain recovery. Different from the soft poly(TA-DIB-Fe) copolymer crosslinked by low-density iron(III)-carboxylate complexes,^[8] the ionic-cluster-toughened poly(TA-DIB-Fe) copolymer exhibited strikingly increased stress-affordability. The creep experiments indicated that only 20% strain was induced after a load of 57.2 kPa for 1 h (Figure S14), while the copolymer with iron(III)-to-TA molar ratio of 1/18000 can only sustain a load of 17.4 kPa for 400 s with a strain over 500%.^[8] Moreover, a cylindrical copolymer can sustain a load of 2 kg, and a copolymer film with a thickness of 2 mm can lift a weight of 4.1 kg (Figure S15). These results indicated the remarkable toughened network of the poly(TA-DIB-Fe) copolymer enforced by the ionic cluster formation.

The toughness of the resulting polymer was further investigated by the stress–strain experiment of a notched copolymer film with a 1/2 width scar. The notch experiments were performed using the copolymer with varied iron contents (1/100, 1/500, 1/1000, 1/18000) at two kinds of strain speeds (20 mm min^{-1} and 50 mm min^{-1}). As a result, all of the samples exhibited similar stretchability at a strain rate of 20 mm min^{-1} (Figure S16). The higher strain rate would decrease the breaking elongation of the notch samples (Figure S17), which supported the proposed energy dissipation mechanism by noncovalent bonds because this noncovalent dissipation process usually exhibits dependence on deformation rates.^[2d] All the samples with varied iron(III) ion contents exhibited considerable anti-tearing ability (Figure S18). For the poly(TA-DIB-Fe) copolymer with an iron(III)-to-TA molar ratio of 1/100, the sample with 1/2 notch can be stretched into over 700% at the strain rate of 50 mm min^{-1} , suggesting that this ionic-cluster-toughened strategy can maintain the anti-tearing ability of the network. Meanwhile, a pre-stretched (200%) copolymer film can be also stretched in the vertical direction (Figure 3 H), which can be self-recovered after release. This process can be repeated several times (Movie S1), showing its good elasticity.

High mechanical strength usually leads to low dynamics and as a consequence inhibits the self-healing capability of materials, which represents a wide trade-off in the design of self-healable materials.^[1f, 2b, 4c, 16] Taking advantage of the interplay of four types of dynamic combinations (i.e. dynamic chemical bonds and non-covalent interactions) in the network, we next focused on studying the self-healing performance of the ionic-cluster-toughened poly(TA-DIB-Fe) copolymer with an iron(III)-to-TA molar ratio of 1/100. We observed that a) A scratch on the copolymer film can be basically repaired at room temperature in 24 h (Figure 4 A);

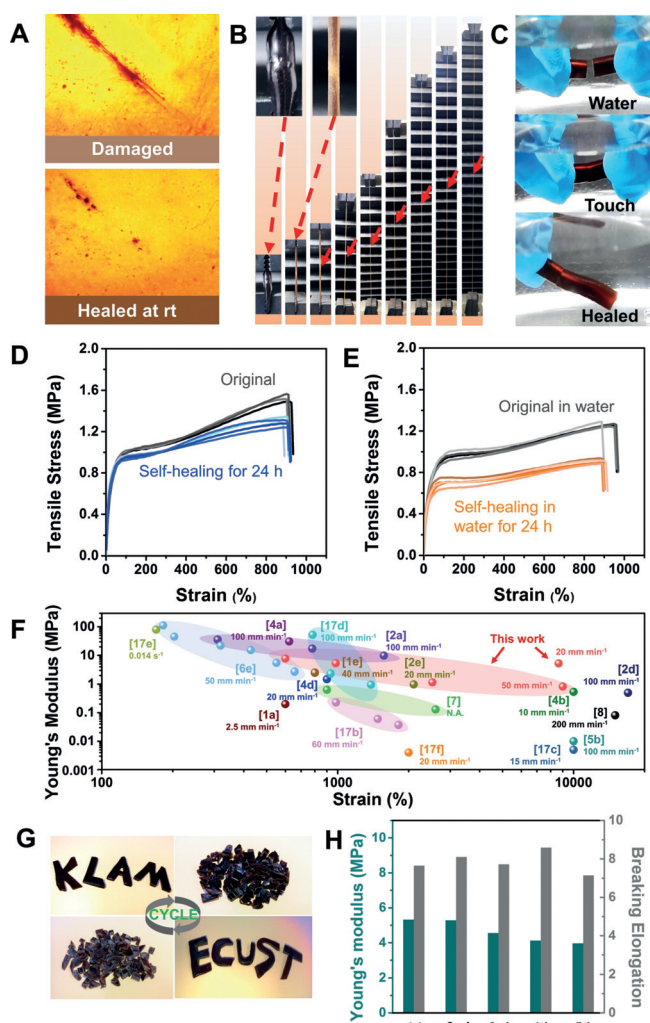


Figure 4. A) Optical microscope images of the damaged and healed polymer showing the auto-restoration at room temperature for 24 h. B) Optical images of poly(TA-DIB-Fe) at different strains with a loading rate of 20 mm min^{-1} . C) Bisected the copolymer cylinder to two pieces and put together under water condition for self-healing. D,E) Stress–strain curves of the original and healed samples of poly(TA-DIB-Fe) copolymer in air (D) and in water (E) for 24 h at room temperature. Parallel self-healing experiments were performed 5 times to show reproducibility. The iron(III)-to-TA molar ratio was 1/100. Tensile speed is 50 mm min^{-1} . F) Comparison of the present system to recent literature studies on self-healable elastomers, which are marked with reference codes and strain rates in the diagram. G) Photographs of the reprocessed polymer with different shapes. H) Mechanical properties of the recycled polymers during five cycles.

b) A cylindrical sample can be healed automatically by contacting the cut interfaces. (Figure S19); c) The healed sample exhibited high stretchability (Figure 4B); d) The self-healing process can be also performed in water (Figure 4C and Movie S2). To quantitatively evaluate the self-healing performance, the stress–strain curve of the healed sample at room temperature after 24 h was tested, showing an excellently recovered mechanical strength and stretchability (Figure 4D, and S20). The self-healing efficiency also exhibited a typical time-dependent feature (Figure S21). This efficient self-healing ability of the resulting copolymer should be

attributed to the synergetic dynamic exchange process of the existing four types of dynamic combinations in the dry network, that is dynamic covalent disulfide bonds, hydrogen bonds, iron(III)-carboxylate complexes, and ionic clusters.

The self-healing ability is usually inhibited by the presence of water especially for H-bond-mediated repairing examples.^[7,16a] The quantitative self-healing experiments were performed in water, and the mechanical tensile test showed a good healing efficiency (Figure 4E), in which the mechanical strength recovered 93.9% of the original moduli and the breaking elongation fully recovered. The good self-healing efficiency under water might be attributed to the presence of dynamic ionic bonds at the interfaces.^[2f,5] To evaluate the water-stability of the ionic-cluster-toughened network, soaking in water for several days led to no swelling or dissolution (Figure S22). Therefore, our copolymer materials simultaneously exhibited high mechanical toughness, high stretchability, and room-temperature self-healing capability. To compare this performance with previous reported materials,^[17] we summarized the modulus (mechanical strength) and breaking elongation (stretchability) of the recently reported synthetic polymer materials that can undergo self-healing at room temperature (Figure 4F). The simultaneous realization of high modulus and breaking elongation in single self-healing material system indicates the effectiveness of the ionic-cluster-toughening strategy in such a solvent-free and dynamic supramolecular network.

Polymers that can be reused in a mild and energy-saving process are of great importance due to rising environmental, materials recycling and energy issues.^[18] The self-healing ability enabled an easy processability of the poly(TA-DIB-Fe) copolymer. The polymer fragments can be remolded into different shapes under given pressure at room temperature for 24 h (Figure 4G). The recycled copolymers by this method showed no remarkable fatigue in mechanical moduli and breaking elongation (Figure 4H), suggesting the great potential of this polymer to be applied in reusable plastics and materials.

In summary, we have demonstrated a toughening strategy for a low-modulus supramolecular network by introducing high-density iron(III)-carboxylate complexes to form secondary ionic clusters. The toughened dry network exhibited remarkably increased mechanical moduli (63 times higher than the original network), high stretchability, self-healing ability at room temperature, water-insensitivity, and reversible processability under mild conditions. This study also supports a successful example in the exploration toward the fundamental question whether high-density metal-ligand combinations could simultaneously facilitate the mechanical properties and self-healing performance of dry polymers. We envision that this low-cost, natural-product-based and high-performance material might play a prominent role in many practical applications, including wearable devices, protective coatings and biomedical materials.

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Conflict of interest

The authors declare no conflict of interest.

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