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## Dynamic poly(disulfide)s for sustainable materials

Deng, Yuanxin

DOI:  
[10.33612/diss.208714129](https://doi.org/10.33612/diss.208714129)

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

*Publication date:*  
2022

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*  
Deng, Y. (2022). *Dynamic poly(disulfide)s for sustainable materials*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen. <https://doi.org/10.33612/diss.208714129>

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## Chapter 5

# Closed-loop Chemical Recycling of Synthetic Polymers by Intrinsically Reconfigurable Poly(disulfides)

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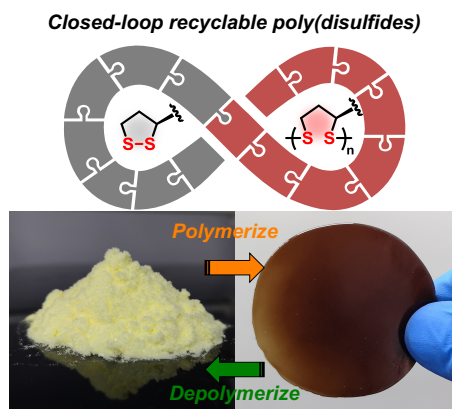
Published as:

*Matter*, **2021**, *4*, 1352-1364 (The depolymerization process of poly(TA-Metal) was include in this chapter).

Qi Zhang, Yuanxin Deng, Chen-Yu Shi, Ben L. Feringa\*, He Tian, and Da-Hui Qu\*

**Abstract:**

The excessive use of plastics has led to severe global problems involving environmental, energy and health issues and demands for sustainable and recyclable alternatives. Towards circular plastics, the development of efficient chemical recycling methods without loss of properties or allowing reprocessing into new materials offer tremendous opportunities. Here, we report an intrinsically recyclable and reconfigurable poly(disulfide) polymer using a natural small molecule, thioctic acid (TA), as the feedstock. Taking advantage of its dynamic covalent ring-opening polymerization, this material enables a dual closed-loop chemical recycling network among TA monomers and two kinds of polymer products, including self-healing elastomers and mechanically robust ionic films. Mild and complete depolymerization into monomers in diluted alkaline aqueous solution is achieved with yields of recovered monomers up to 86%. The polymer materials can be repeatedly recycled and reused with reconfigurable polymer composition and tunable mechanical properties offering prospects for sustainable functional plastics.



## 5.1 Introduction

Non-recyclable plastics have aroused increasing global attention because of the involved environmental damage and have led to a growing awareness to re-use materials.<sup>1</sup> Although some fine examples of sustainable polymers have been developed,<sup>2,3</sup> high cost of production and recycling as well as limited applicability hampers the replacement of common plastic materials<sup>4-6</sup> and in fact only about 9% of the plastics in the United States and 15% in Europe are currently recycled.<sup>7</sup> Until now a main recycling method involves mechanical reprocessing, which is applied to thermoplastics and cannot avoid the dramatic loss of mechanical properties after several cycles.<sup>8</sup> Mechanical reprocessing does not remove or change the extra additives such as colorants in the plastics, unless solvent washing procedures are applied.<sup>5</sup> These disadvantages make that the current “recyclable” plastics are mostly down-cycled into products with lower-value applications.<sup>7</sup>

In contrast, chemical recycling strategies make it possible to regenerate monomeric feedstock by depolymerizing plastics waste.<sup>9-19</sup> The polymer products, based on recovered monomers, can be exactly the same as the original ones or even reproduced to materials with distinct properties. In an ideal chemically circular system, the cycle of “feedstocks-products-wastes” can be self-sustained in a closed loop.<sup>15</sup> Towards this goal, chemists have exploited a few successful systems for chemical recycling of synthetic polymers based on specific catalyst design<sup>9-11</sup> or constructing reversible co-polymer networks by dynamic covalent chemistry.<sup>12-14</sup> However, to the best of our knowledge, it remains highly challenging to realize chemically recyclable homo-polymers avoiding costly tedious synthesis of monomers. Meanwhile, towards a sustainable future, “green” plastics should also exhibit environmentally friendly preparation, minimal benign material and function-enhancing performance.<sup>20</sup>

Here we demonstrate, using a natural small-molecule monomer thioctic acid (TA), the closed-loop chemical recycling of TA-based polymers by ring-closing depolymerization. The recycling process features low cost, high yield and scalability, avoids the use of organic solvents and is additive-tolerable. Importantly, two types of polymeric materials share the same feedstock i.e. the recycled TA monomer, enabling a dual closed-loop chemical interconversion towards elastic self-healing



polymers, as well as mechanically robust ionic networks through a cascade of several cycles.

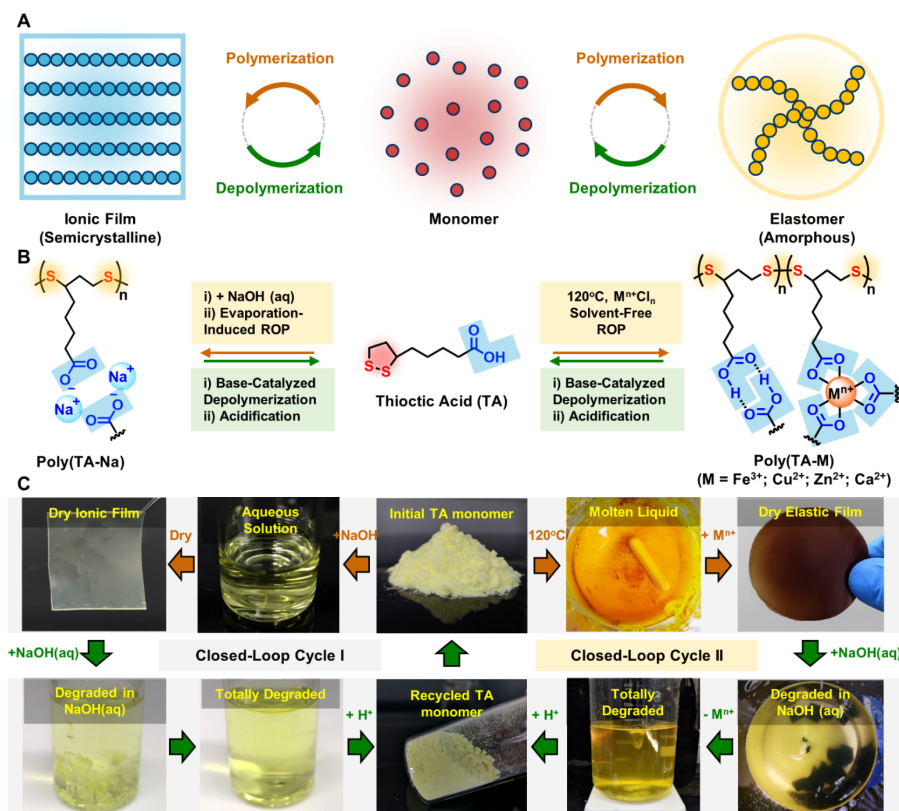
## 5.2 Results and Discussion

### 5.2.1 Preparation and chemical structure of homopolymers

In recent studies,<sup>21-23</sup> we have demonstrated two different pathways for dynamic covalent ring-opening polymerization (ROP) of natural monomer thioctic acid (TA): i) Low-melting-point TA can be directly transformed into a thermoplastic elastomers by one-step solvent-free melting process;<sup>21,23</sup> ii) Hydrophobic TA can be transformed into water-soluble sodium salt (TA-Na) after deprotonation by sodium hydroxide. The aqueous solution of TA-Na monomers can be directly transformed into mechanically robust semi-crystalline network by evaporation-induced interfacial self-assembly (EIISA).<sup>22</sup> The resulting polymers exhibited excellent mechanical properties enabling various potential applications, such as self-healing materials, elastomers, and actuators.<sup>21-23</sup> It should be noted that in order to facilitate recyclability involving polymerization and de-polymerization, reactions closer to equilibrium are needed and the intrinsically dynamic disulfide bond<sup>24</sup> within the five-membered ring of TA not only offers a chance to enable dynamic properties of polymers but also facilitates the control of polymerization and de-polymerization by chemical means.<sup>25-31</sup>

The naturally tailored structure of our monomer TA features a disulfide five-membered ring, which facilitates reversible interconversion between monomers and polymers, as it is activated by strain in the five-membered ring, with intrinsic lower bond energy than present in traditional open-chain disulfide bonds.<sup>32</sup> This allows TA to readily polymerize under conditions of i) high concentration to favor intermolecular reactions, and ii) external stimulus to activate the disulfide bond, such as heat,<sup>21,23,33,34</sup> light,<sup>32,35</sup> and base.<sup>36</sup> Efficient polymerization of TA can be easily realized by the two methods we developed previously, namely heat-induced dynamic covalent ROP in a solvent-free condition,<sup>21,23</sup> and EIISA from aqueous solution.<sup>22</sup> To enable and maximize the recyclability of the TA-based polymer system, the previously employed crosslinker,<sup>21,23</sup> 1,3-diisopropenylbenzene (DIB), was avoided because its irreversibly covalent copolymerization would inhibit recycling efficiency. We now found that the poly(TA) network in the absence of DIB can also be stabilized as a homogeneous polymer film by adding metal ions (1% molar ratio of TA), such

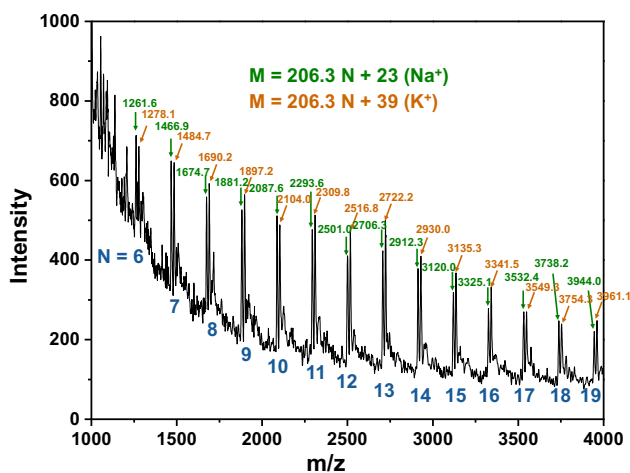
as  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ca}^{2+}$ . Thus, amorphous poly(TA) homo-polymer instead of co-polymer can be readily prepared by a solvent-free melting method by mixing with specific amounts of metal salts (Fig. 5.1). We anticipate that high-concentration metal ions form secondary ionic clusters to toughen the solvent-free network of poly(TA),<sup>23</sup> thus inhibiting the “back-bite” depolymerization process by limiting the mobility of polymer chains.



**Figure 5.1** The dually closed-loop recycling network of TA-based polymers. (A) The schematic representation of the interconversion among monomers and two kinds of polymeric products, i.e. ionic film and amorphous elastomers; (B) Molecular structures of TA monomer and two kinds of polymers; (C) Photographs of the dual closed-loop recycling steps of poly(TA) homopolymers. The preparation (polymerization) process of cycle I involves the dissolution of TA monomers in aq. NaOH solution, followed by water evaporation on surface, forming dry ionic poly(TA-Na) film. The preparation (polymerization) method of cycle II includes the solvent-

free melting of TA monomers and then the addition of metal salts, resulting in dry elastic poly(TA-M) ( $M = \text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ) films after cooling to room temperature. The depolymerization process of the two polymer materials is performed in alkaline aqueous solutions (0.5 M NaOH aqueous solution), and the recovered monomers can be separated by precipitation after acidification, enabling the polymer system to be circularly sustainable.

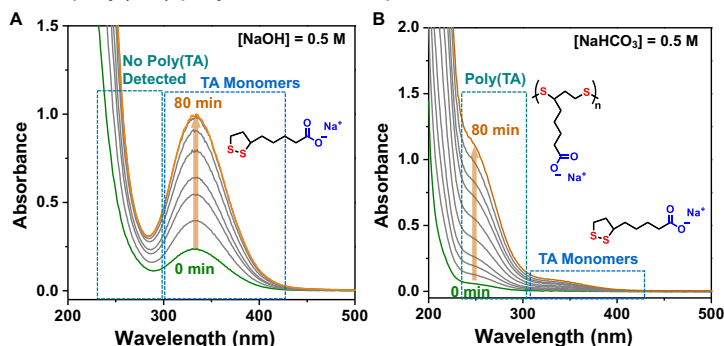
The homopolymer structure was confirmed by nuclear magnetic resonance  $^1\text{H}$  NMR (Fig. S1) and the polymer topology was revealed as cyclic polymers by matrix-assisted laser desorption-ionization time of flight mass spectrometry (MALDI-TOF-MS) (Fig. 5.2). The supramolecular network showed insolubility in water and solubility in polar organic solvents (Fig. S2). The resulting poly(TA-M) polymers exhibited good mechanical properties (Fig. S3), including tunable Young's moduli of 160 ~ 660 KPa depending on the nature of the metal ions, as well as excellent stretchability over 6000% in all poly(TA-M) samples (Fig. S3). The stretchability was attributed to the existence of energy dissipation mechanism in the hierarchically assembled supramolecular network (i.e. dynamic nature) containing H-bonds, and metal-carboxylate complexes.<sup>21,23</sup>



**Figure 5.2** MALDI-TOF analysis of the resulting poly(TA-Fe) homopolymers. The iron ions and existed monomers were washed by a large amount of acetonitrile to produce pure poly(TA) homopolymer, a sticky white solid. The polymer solid can be dissolved in ethanol by continuously stirring.

### 5.2.2 Base-mediated depolymerization

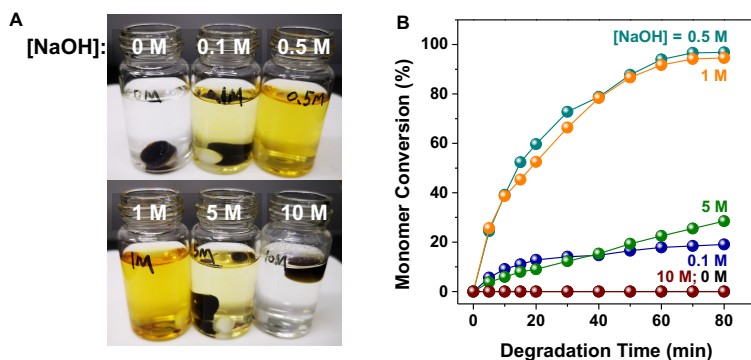
In contrast to the polymerization conditions, depolymerization of poly(TA) requires diluted conditions and activation of the disulfide bonds. Using simple inorganic base as a catalyst for the disulfide exchange reaction<sup>36</sup> and water as a preferred solvent due to its environmental friendly nature, we developed a low-cost recycling system to depolymerize poly(TA) polymers in an aqueous alkaline solution.



**Figure 5.3** Base-mediated depolymerization of the poly(TA-Fe) homopolymers. (A-B) Real-time detected UV-Vis spectra of the aqueous solution of the degraded poly(TA-Fe) network catalyzed by different base, NaOH (A) and NaHCO<sub>3</sub> (B). Both base concentrations were 0.5 M.

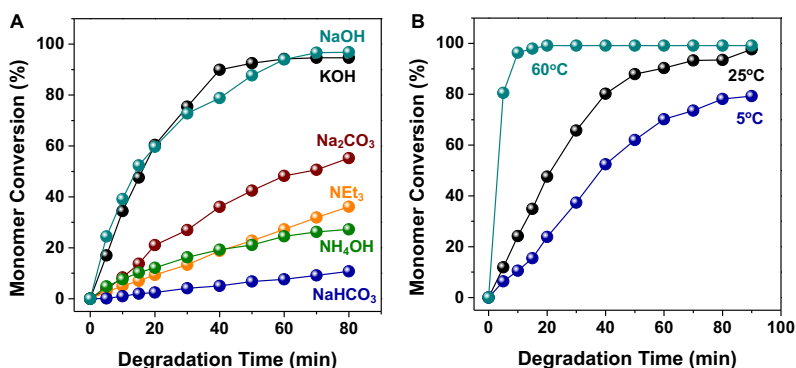
We first tested the base-mediated depolymerization of poly(TA-Fe) (molar ratio of iron(III) to TA is 1:100) by immersing a piece of polymer sample into 0.5 M aq. NaOH solution. Upon stirring at room temperature, the solution became yellow and the polymer sample gradually dissolved. To confirm depolymerization rather than simple dissolution, monomer formation was detected in real time by UV-Vis spectroscopy of the solution (Fig. 5.3A). An absorption peak at 330 nm appeared immediately after immersing the polymer into NaOH aqueous solution, and showed increasing intensity with reaction time, which was attributed to the distinctive absorption peak of the disulfide bond in the closed-ring TA monomer.<sup>32</sup> Full conversion was reached in 70 min (Fig. 5.3A). The disulfide bond in poly(TA) polymers shows a blue-shifted absorption peak at 250 nm.<sup>33</sup> The solution after depolymerization showed no visible “shoulder” peak of poly(TA) (Fig. 5.3A), indicating the complete degradation of poly(TA) in the aqueous solution of NaOH. Interestingly, the polymer could also be dissolved in an aqueous solution of the weak base NaHCO<sub>3</sub>, but no yellow color was observed in the solution. UV-Vis spectra showed a distinctive absorption maximum

at around 260 nm attributed to poly(TA), and the low-intensity monomer absorption at 330 nm indicated the slower depolymerization (10% conversion after 80 min) catalyzed by weak base  $\text{NaHCO}_3$  (Fig. 5.3B). These results revealed that in alkaline aqueous solution the crosslinked poly(TA-Fe) network is readily converts into monomers and the base-catalyzed depolymerization process is accelerated by a stronger base.



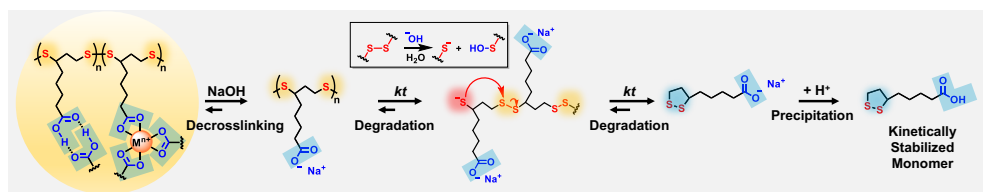
**Figure 5.4** Photographs (A) and kinetic curves (B) of the degraded mixtures of poly(TA-Fe) network in aqueous solutions with different concentrations of NaOH (0 M, 0.1 M, 0.5 M, 1 M, 5 M, 10 M).

Furthermore, the depolymerization kinetics of poly(TA-Fe) homopolymers was tested with different concentrations of aq. NaOH (Fig. 5.4A-B). The polymer sample showed no detectable degradation in water in the absence of NaOH. The degradation rate increased with increasing NaOH concentrations (0 M to 0.5 M). In sharp contrast, at concentrations over 0.5 M, the degradation rate showed a remarkably negative correlation with the concentration of NaOH (Fig. 5.4B) and especially no degradation or even any dissolution was observed with 10 M aq. NaOH. At this high concentration the polymer sample was found to float in the solution (Fig. 5.4A). The lack of degradation was attributed to the decreased solubility of poly(TA-Fe) homopolymer in water due to the drastically increased ionic strength, which also revealed the important rate-limiting role of the dissolution process of the poly(TA-Fe) network in alkaline aqueous solution. The depolymerization of the poly(TA-M) network was also confirmed when the iron(III) ion was replaced by other metal ions, including  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ . The kinetic curves of degradation of these four species of poly(TA-M) were found to be similar (Fig. S4).



**Figure 5.5** (A) Kinetic curves of the monomer conversion percentages in aqueous solution of different bases. All of the base concentrations were 0.5 M; (B) Temperature-dependent kinetic curves of the monomer conversion percentages of poly(TA-Fe) in 0.5 M aq. NaOH solution.

Different types of bases were used for depolymerization, revealing that degradation kinetics exhibited a positive correlation with the basicity (Fig. 5.5A). Meanwhile, higher temperatures were found to accelerate the degradation rate of poly(TA-Fe) in aq. NaOH solution (Fig. 5.5B). The time for complete degradation was shortened to 20 min at 60°C, exhibiting a highly efficient depolymerization process in water. The degradation rate showed a positive correlation with the reactive surface area of the polymer samples (Fig. S5), indicating the important role of surface diffusion in this heterogeneous degradation process.



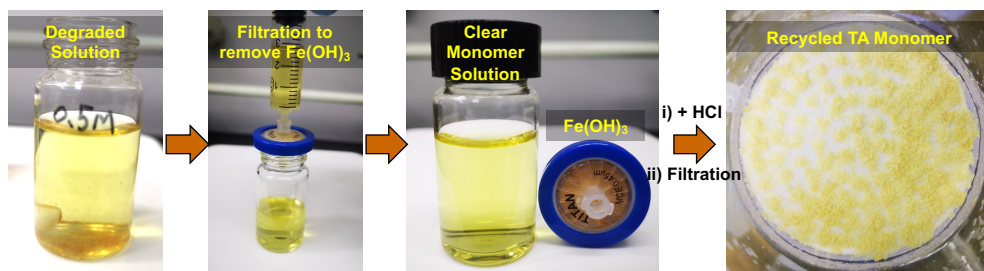
**Figure 5.6** Proposed degradation mechanism of the network in an alkaline aqueous solution.

Based on these findings, a two-step degradation mechanism is proposed (Fig. 5.6): i) The hydrogen bonds and iron(III)-carboxylate complexes are “de-crosslinked” by deprotonation or formation of metal hydroxide aggregates using hydroxide base. This de-crosslinking step enables the complete dissolution of poly(TA-Fe) polymers from the solid network into water-soluble polymer chains. ii) Ring-closing

depolymerization of poly(TA) homopolymers is catalyzed by the terminal thiolate groups (Fig. 5.6), which are formed by base-induced disulfide scission.<sup>36</sup> As a consequence, poly(TA-M) ( $M = \text{Fe}^{3+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Ca}^{2+}$ ) elastomers can be completely degraded into TA monomers by simply stirring the samples in low-concentration aq. NaOH solutions.

### 5.2.3 Chemically recycling of the monomers

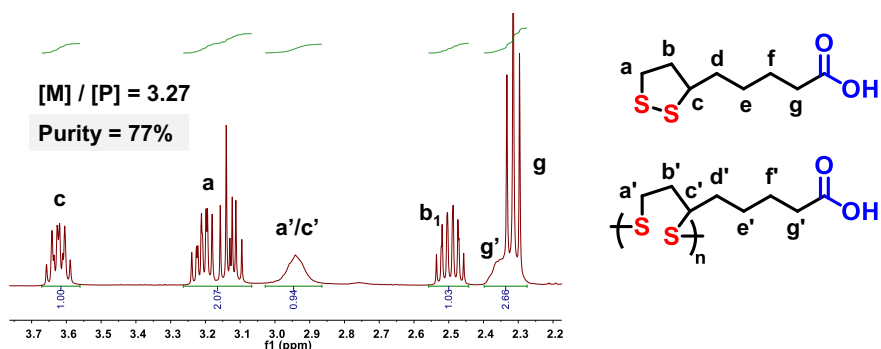
The next important step is the separation and purification of TA monomers from the de-polymerization mixtures. As the degradation products of poly(TA-Fe) elastomers consist of water-soluble deprotonated TA monomers and  $\text{Fe}(\text{OH})_3$  precipitates, the red brown solid  $\text{Fe}(\text{OH})_3$  can be easily removed from the mixture by filtration (Fig. 5.7). Then the transparent filtrate containing TA monomers and excess base was acidified ( $\text{pH} = 3 \sim 4$ ) by aq. hydrochloric acid (1 M) to protonate and precipitate the TA monomers as yellow powders (Fig. 5.7) in yields of about 60% ~ 80%. The isolation yield presented a negative correlation with the concentrations of TA monomers at the acidification step (Fig. S6).



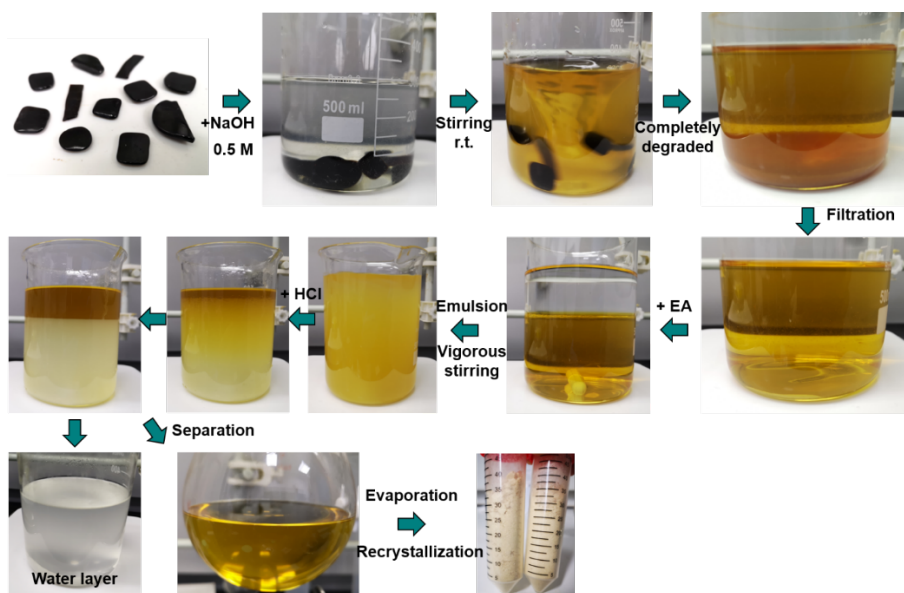
**Figure 5.7** Chemical recycling of the degraded monomers. Photographs of the facile purification procedure of TA monomers from the degraded mixture.

The loss of unrecycled TA monomers was attributed to the existence of spontaneous polymerization at the acidification step forming oligomeric colloids, which couldn't be fully collected by filtration, as revealed by i) the turbid white filtrate after acidification, and ii) the observed polymer/oligomer optical absorption peak at 250 nm of the separated TA solids (Fig. S7). The composition of the recycled yellow solids by this method was confirmed as 77% TA monomers containing 23% soluble poly(TA) by analysis of  $^1\text{H}$  NMR spectra (Fig. 5.8).





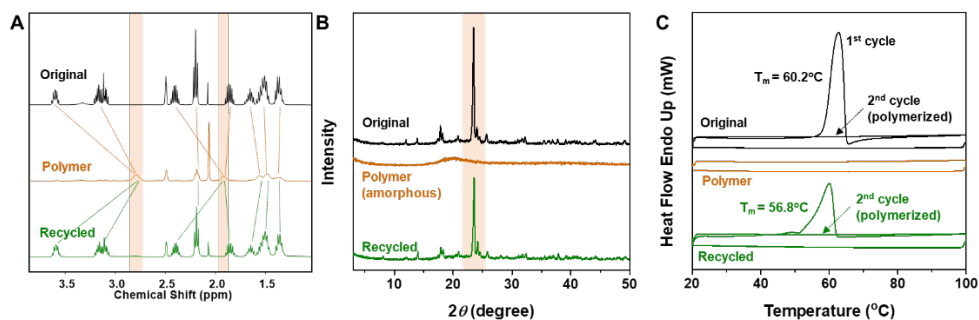
**Figure 5.8** Partial  $^1\text{H}$  NMR spectra of recycled TA monomers obtained by direct acidification. The purity of monomers was calculated by the integral ratio of distinctive peak of proton  $\text{H}_a$  and  $\text{H}_c$ . (400 MHz, 298 K,  $d_6$ -DMSO).



**Figure 5.9.** Photographs of the recycling experiments using extraction-assisted acidification by ethyl acetate (EA). Before acidification step, 1/2 volume equivalent EA was added to form emulsion mixture by vigorous stirring. Then aqueous HCl solution was added into the emulsion mixture to tune the pH down to 3. The resulting mixture was standing without stirring to form clear oil/water interface. The EA layer was collected and concentrated by evaporation. A yellow solid with virgin quality was obtained by recrystallization in hexane. The isolation yield of the recycled TA was 86%.



To avoid this side reaction, an effective solution was to form a two-phase emulsion by adding ethyl acetate before acidification. This method allowed the immediate extraction of the protonated TA monomers from the water phase to organic phase without any precipitation and avoided polymerization induced by aggregation. This method afforded TA as a highly pure solid in a yield of 86%. Thus, the two procedures for the acidification, isolation steps led to a trade-off between monomer quality/yield and technical cost/sustainability: the direct acidification method avoided the use of organic solvents, but also resulting in the slight loss of isolated yield and monomer purity. However, taking advantage of dynamic covalent polymerization of TA, the existence of poly(TA) oligomers in the recycled TA solids would not lead to quality reduction of poly(TA-M) elastomers. The “self-repairing” self-assembly mechanism would drive the dynamic system into the same final state,<sup>37,38</sup> that is thermodynamically controlled nature. Hence, considering the importance of sustainability and environmental friendliness, a direct acidification process without extraction by organic solvents is preferred for our polymer recycling system, although the extraction method also offered an effective way to recycle TA monomers to yield high quality crystalline material. To verify the potential for industrial application, large-scale (100 g) polymerization and recycling experiments have been successfully performed (Fig. S8 and 5.9), revealing the practicality of this recyclable polymer system.

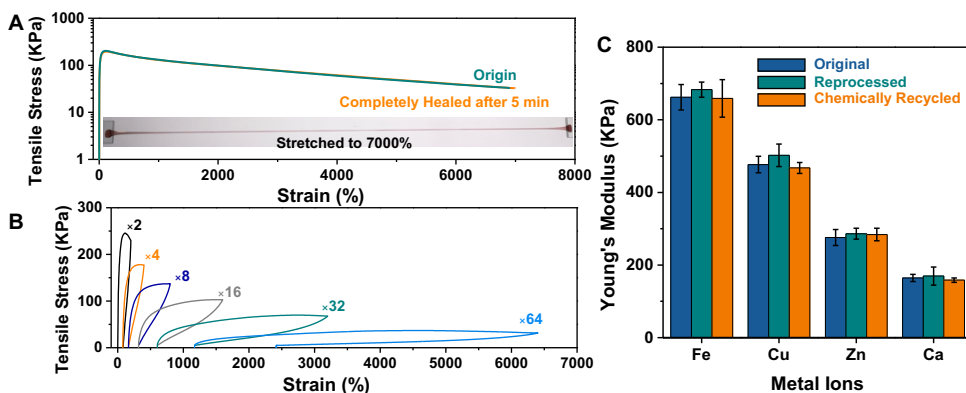


**Figure 5.10** (A) Partial  $^1\text{H}$  NMR spectra of virgin feedstock, poly(TA-Fe) homopolymers, recovered monomers by extraction-assisted acidification method. The  $^1\text{H}$  NMR spectrum of the monomers recovered by direct acidification method can be found in Fig. 5.8; (B-C) Comparison of virgin feedstock, poly(TA-Fe) homopolymers, and recovered monomers by direct acidification method, by XRD (B) and DSC measurements (C).

To further confirm the successful recycling of TA monomers, we compared the original feedstock and recycled monomer of TA by  $^1\text{H}$  NMR, X-Ray diffraction (XRD), and differential scanning calorimetry (DSC).  $^1\text{H}$  NMR spectra showed pure TA monomers obtained by acidification with extraction (Fig. 5.10A), while the recycled TA solids obtained by direct acidification without extraction contained 23% oligomer species (Fig. 5.8). Furthermore, the sharp and consistent diffraction peaks in XRD indicated high crystallinity of the TA monomers recycled by direct acidification (Fig. 5.10B). Moreover, the DSC curve of TA monomers recycled by direct acidification showed a slightly shifted melting peak at  $56.8^\circ\text{C}$  compared with the original feedstock, as well as the ability of melting-induced polymerization evident from the absence of melting peak at the second heating cycle (Fig. 5.10C). These combined results unequivocally demonstrated the successful chemical recycling of TA monomers from their homopolymers.

#### **5.2.4 Mechanical properties of the recycled polymers**

Mechanical properties are of great importance for the practical applicability of polymer materials<sup>40, 41</sup> and we examined both physical and chemical reprocessing. A key problem of plastic reprocessing technology rests on the inevitable fatigue on mechanical performances of the recycled products, resulting in down-cycled applications and a notable value loss.<sup>7,8</sup> The TA-based polymer showed excellent capability to circumvent the mechanical fatigue problem using both physical reprocessing or chemical recycling methods. The thermoplastic poly(TA-Fe) network exhibited excellent self-healing properties as the healed sample showed completely recovered stiffness and stretchability after contacting the cut interfaces and allow it the material standing for 5 min under ambient condition (Fig. 5.11A and S9). The self-healing ability of poly(TA-Fe), including completeness and efficiency, was remarkably increased compared to our previously reported poly(TA-DIB-Fe) network,<sup>23</sup> which is attributed to the dynamic network entirely comprising crosslinking by supramolecular interactions, i.e. hydrogen bonds, and metal-carboxylate complexes. The complete self-healing ability endowed the poly(TA-Fe) network also with fatigueless mechanical processability. A transparent film could be reformed in 2 h from polymer fragments by simple physical extrusion (about 3 bar) at ambient conditions (Fig. S10).



**Figure 5.11** Mechanical properties of reprocessed and chemically recycled polymers. (A) Stress-strain curves of poly(TA-Fe) before and after healing with fresh cut interfaces. Inset photograph showed the long filaments stretched to 70 times of the original length; (B) Sequential loading-unloading stress-strain curves with no rest intervals of the reprocessed poly(TA-Fe) sample, which was made from the mechanical extrusion of the polymer fragments; (C) Young's modulus of virgin samples, reprocessed samples and chemically recycled samples.

The reprocessed polymer membrane showed excellent stretchability in multi-step cyclic tensile experiment (Fig. 5.11B). Samples after reprocessing still exhibited consistent mechanical performances compared to the virgin material (Fig. 5.11C), suggesting excellent reprocessability. Similar self-healing ability and reprocessability was also observed in poly(TA-M) ( $M = \text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ) networks (Fig. 5.11C and S11). Meanwhile, recycling involving physical reprocessing does not allow the upcycling of the material by reconfiguring the external additives such as metal ions. Therefore, chemical recycling is still necessary to make this polymer system truly sustainable in terms of dual closed-loop recycling.

As demonstrated above, chemical recycling efficiently transformed the two types of TA-based polymers, i.e. poly(TA-M) ( $M = \text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ) elastomers, into TA monomers without metal residues. Considering the presence of small portions of oligomers formed in the direct acidification process, the mechanical properties of the polymer samples reformed by the recycled TA monomers were tested, showing that the thermoplastic poly(TA-M) elastomers had fully recovered mechanical Young's moduli (Fig. 5.11C). The consistent mechanical performance of the chemically

recycled polymers indicated that the dynamic covalent “self-repairing” mechanism of this polymer system enables fully recovered products despite the slight amounts of oligomers present in the recycled feedstock.

### **5.3 Conclusions**

In summary, we have presented a versatile polymer system with closed-looped recyclability, based on the versatile dynamic covalent chemistry of a natural small molecule TA. Thermoplastic poly(TA-M) elastomers can be recycled into TA monomers by degrading in diluted NaOH aqueous solution and monomers are isolated in high yield. The chemical recycling method is highly efficient, fast depolymerization rate, mild conditions, high quality recycled monomers, low-cost, energy-saving, and scalable, and meanwhile the use of organic solvent can be avoided enhancing its environmentally friendly nature. Unique features include reproducing capability (simply changing metal ions), self-healing properties and dual-mode closed-loop recycling producing soft and hard materials in multiple subsequent cycles. Combined with the broad tunability of mechanical properties, this polymer system simultaneously exhibited synthetic simplicity and functional complexity. We foresee that this study could pave the way to the development of chemically recyclable synthetic plastics<sup>42</sup> and represent a vital step of TA-based polymers towards future high-performance and sustainable materials.

### **5.4 Acknowledgements and Contributions**

This work was supported by National Natural Science Foundation of China (grants 22025503, 21790361, 21871084, 21672060), Shanghai Municipal Science and Technology Major Project (Grant 2018SHZDZX03), the Fundamental Research Funds for the Central Universities, the Programme of Introducing Talents of Discipline to Universities (grant B16017), Program of Shanghai Academic/Technology Research Leader (19XD1421100), and the Shanghai Science and Technology Committee (grant 17520750100). B. L. Feringa acknowledges the financial support of the Netherlands Ministry of Education, Culture and Science (Gravitation program 024.601035). Y. Deng acknowledges the financial support of China Scholarship Council. We thank the Research Center of Analysis and Test of East China University of Science and Technology for help on the material characterization.

Y.D. synthesized the poly(TA-M)s, conducted experiments on chemical recycling, mechanical recycling, tensile testing on poly(TA-Fe) and contributed to the manuscript. Q.Z. devised, guided the project, conducted experiments on chemical recycling and wrote the manuscript. C.S. synthesized the poly(TA-Na)s and assisted the characterization of materials. B.L.F, H.T. and D.H.Q guided the project and contributed to the manuscript.

## 5.5 Experimental Section

### 5.5.1 Materials

All the reagents were purchased from Adamas@beta, TCI and Sigma-Aldrich. The key feedstock ( $\pm$ )- $\alpha$ -thioctic acid (TA) was used as received from Adamas@beta with a Reagent Grade (99%). It should be noted that the feedstock of TA should be stored below 4oC in dark to prevent automatic polymerization. Metal salts were used as iron(III) chloride hexahydrate, copper(II) chloride dihydrate, zinc chloride, calcium chloride from Adamas@beta with a Reagent Grade (99%). Ultrapure water (18.2 M $\Omega$  cm) was obtained from a Millipore system (Labconco, Kansas City, MO, USA).

### 5.5.2 Characterization methods

NMR spectra were acquired by a Brüker AV-400 spectrometer using tetramethylsilane as the internal standard. The thermal properties were measured by differential scanning calorimetry (DSC 8500, PerkinElmer). Polymer information was collected by matrix-assisted laser desorption/ ionization time of flight mass spectrometry (MALDI-TOF-MS, ABS, Singapore). X-ray diffraction experiments were undertaken on a rotating anode X-ray powder diffractometer (18KW/D/max2550VB/PC) equipped with a copper target 18 KW (450 mA), a fully automated curved (plate) crystal graphite monochromator and a programmed variable slit system. UV-Vis absorption spectra were collected on an Agilent Cary 60 spectrometer.

### 5.5.3 Synthesis of Poly(TA-M) elastomer

The poly(TA-M) (M = Fe<sup>3+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>) elastomers were prepared according to the previous procedures with partial modifications.<sup>21,23</sup> In a typical experiment, TA powder (5 g) was added into a vial and then heated at 120°C in an oil bath, resulting

in a yellow transparent liquid. Then a magnetic stirrer was used to shear the liquid in a gradually increasing speed. Metal chloride salts (1% molar ratio of TA monomers) were dissolved in minimal corresponding low-boiling-point solvents (acetone or ethanol), followed by their slow injection into molten TA liquid under violent stirring. After getting homogenization, the liquid was poured into a desired mold, and cooled down to room temperature, forming an elastic solid polymer as the poly(TA-M) elastomer.

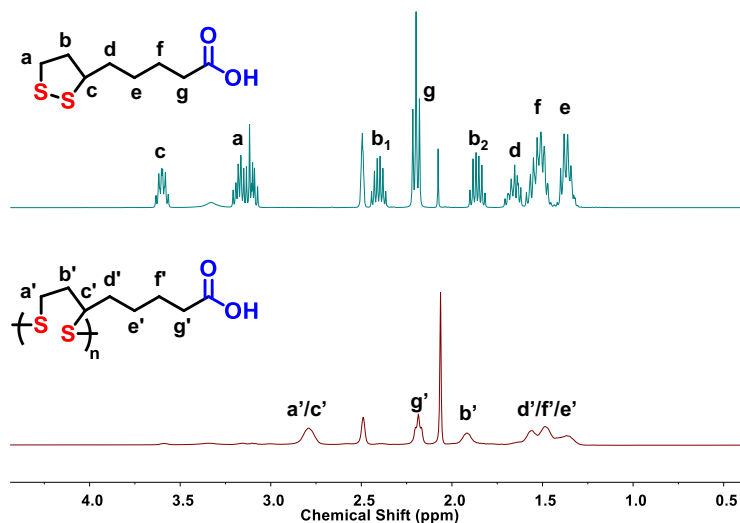
#### **5.5.4 Chemical recycling of polymers**

The chemical recycling procedures consisted of two steps, degradation in basic aqueous solution and separation by acidification. The degradation process only involved the continuous stirring of polymer samples in specific basic aqueous solutions, in which 0.5 M aq. NaOH solution was used, unless indicated otherwise. The volume of aq. NaOH solution was used as 15 mL for every 1 g polymer sample. After complete degradation, the mixture solution was filtrated to remove the formed metal hydroxide precipitates. The filtrate was then acidified to pH = 3 ~ 4 by aq. HCl (1 M) to precipitate TA monomers as yellow powders. Notably, a slow addition of acid would facilitate the obtaining of TA powders with higher purity to inhibit spontaneous polymerization. The spontaneous polymerization during the acidification process can be effectively avoided by adding 1/2 volume equivalent of ethyl acetate before acidification. The formation of two-phase emulsion by vigorous stirring enables the immediate extraction of protonated TA monomers from water phase into organic phase. The organic phase was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, and then mixed with hexane to recrystallize to form virgin-quality TA monomers.

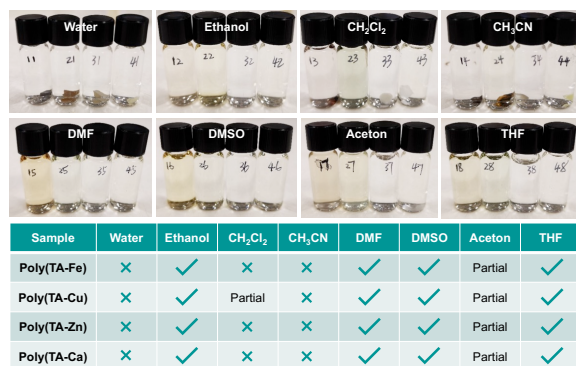
#### **5.5.5 Methods for mechanical test**

All stress-strain curves were collected by an HY-0580 tension machine (HENGYI company, China) connected with a computer. The polymer sample was cut into rectangle pieces (length/width = 20 mm/8 mm). The thickness (0.6 ~ 0.8 mm) of the sample was tested by a screw-thread micrometer. Then the samples were fixed onto the jigs of the machine directly or mediated by two glass slices. The initial length was set as 10 mm by adjusting the gap distances of the jigs or the glass slices. The tensile stress was measured with a constant speed of 50 mm/min for poly(TA-M) elastomers.

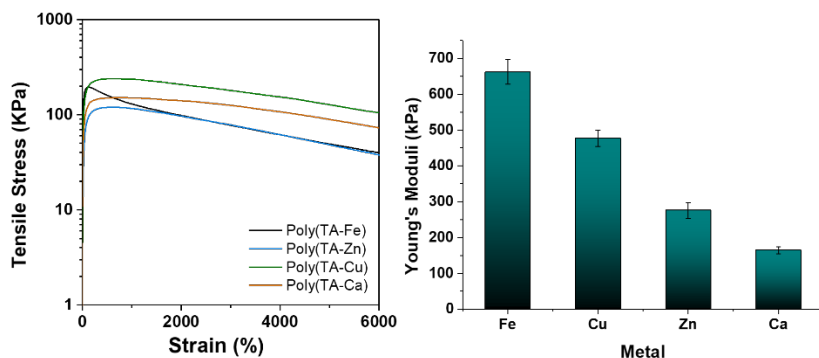
## 5.6 Supplemental Figures



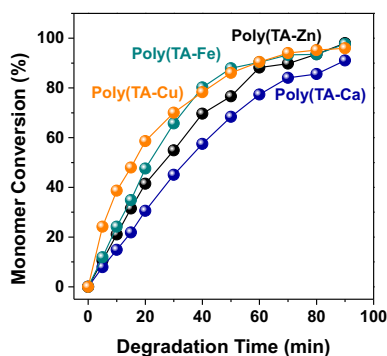
**Figure S1.** Partial  $^1\text{H}$  NMR spectra (400 MHz, 298K,  $d_6$ -DMSO) of TA monomer and poly(TA-Fe) homopolymer. The polymer solution was obtained by dissolving polymer samples in  $d_6$ -DMSO solvent under stirring for 2 h.



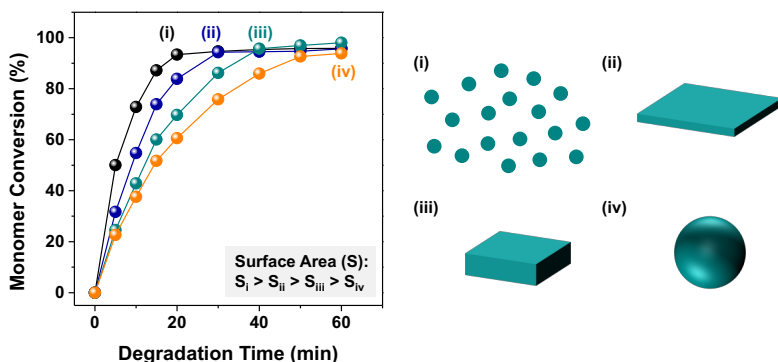
**Figure S2.** Solubility tests of the as-prepared poly(TA-M) network.



**Figure S3.** Tensile stress curves and Young's moduli comparison of poly(TA-M) (M = Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ca<sup>2+</sup>) homopolymers. The tensile stress was measured with a constant speed of 50 mm/min.

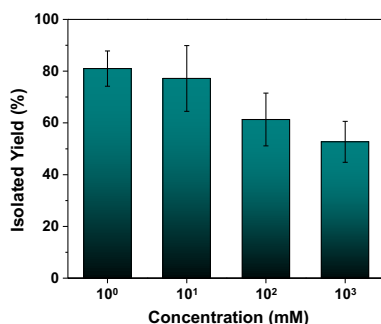


**Figure S4.** Kinetic curves of the monomer conversion percentages of poly(TA-M) samples with different metal ions. [Metal ion] = 1%; [NaOH] = 0.5 M; 25°C.

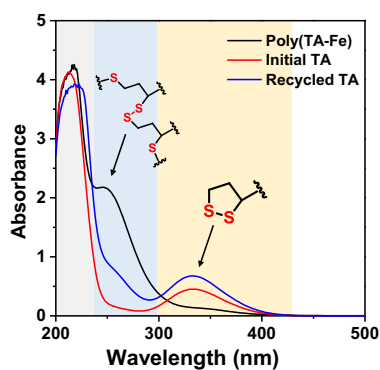


**Figure S5.** Kinetic curves of the monomer conversion percentages of poly(TA-Fe) samples with different surface areas. [NaOH] = 0.5 M; 25°C.

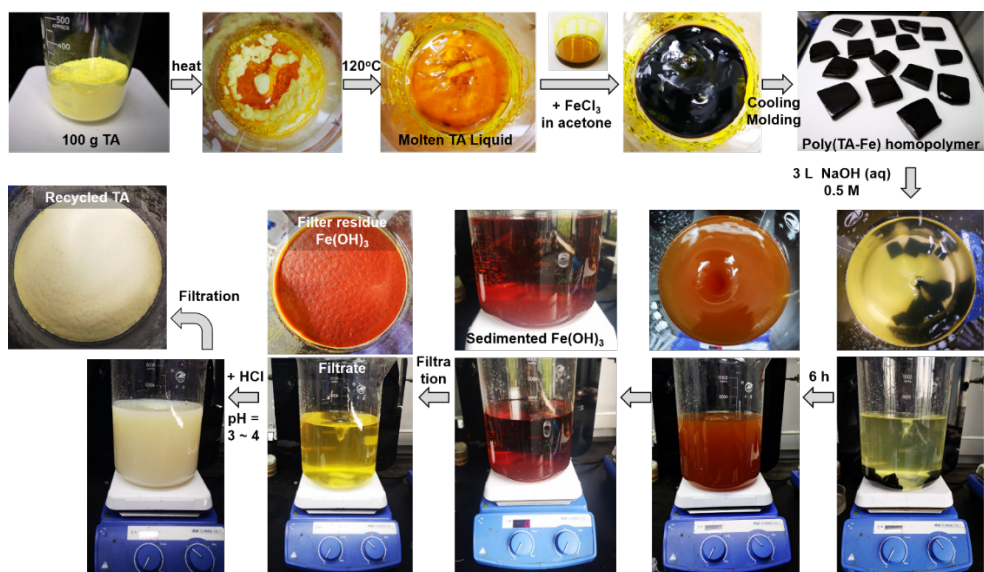




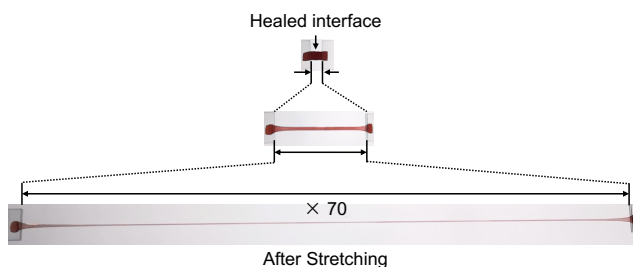
**Figure S6.** Isolated yields obtained by direct acidification of different concentrations of degraded mixtures. The concentrations referred to the molar concentrations of TA monomers before acidification. The yield was calculated by the weight of dry samples.



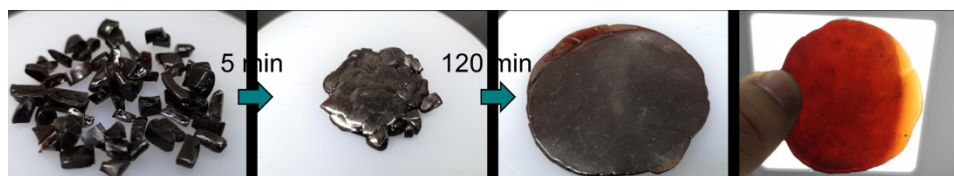
**Figure S7.** UV-Vis absorption spectra of the original TA monomers, poly(TA-Fe) homopolymer, and TA monomers recovered by the direct acidification method. The existence of poly(TA) species in the recycled samples was introduced at the direct acidification step.



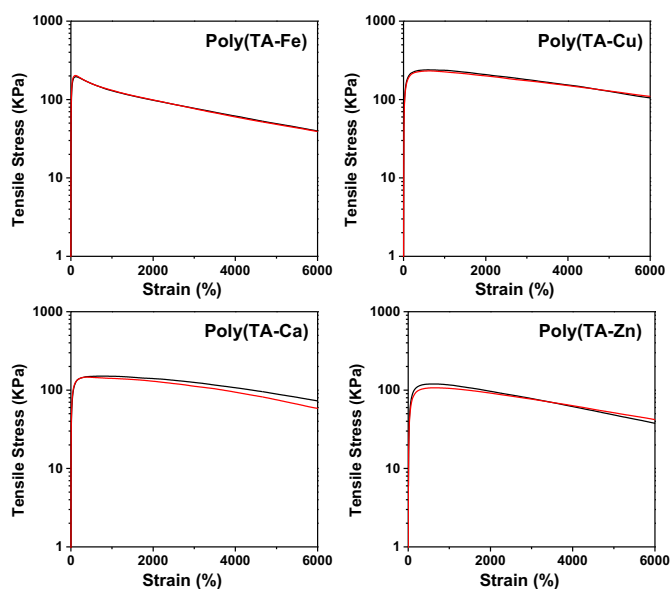
**Figure S8.** Photographs of the large-scale (100 g) polymerization/recycling experiments. TA powder (100 g) was placed in a 500 mL beaker, heated by oil bath at 120°C. After the complete melting of the powder,  $\text{FeCl}_3$  dissolved in acetone was added under vigorous stirring, forming dark red mixture. Then stirring at 120°C for 5 min made the mixture homogenous, followed by pour into molds to cool down to room temperature slowly, resulting dark brown poly(TA-Fe) elastomers. The recycling process involved the immersing of polymer solids into the NaOH aqueous solution (0.5 M, 3L), and the subsequent continuous stirring under ambient conditions. The complete degradation was completely in 6 h, resulting in turbid red mixture. After free sedimentation for 1 h, the red precipitates were separated by pouring and filtration, forming yellow transparent filtrate, which was further acidified by HCl aqueous solution ( $\text{pH} = 3$ ) to precipitate the monomers. Finally, the monomers were recovered by filtration, washing by water, and dried at vacuum. The isolation yield of the recycled TA was 63%.



**Figure S9.** Photographs of the healed poly(TA-Fe) elastomer stretched into 7000% of the original length without breaking.



**Figure S10.** Photographs of the mechanical reprocessing process of poly(TA-Fe) homopolymers.



**Figure S11.** Tensile stress curves of poly(TA-M) (M = Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ca<sup>2+</sup>) homopolymers before (black line) and after (red line) self-healing for 5 min at ambient conditions.

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