

University of Groningen

## Dual closed-loop chemical recycling of synthetic polymers by intrinsically reconfigurable poly(disulfides)

Zhang, Qi; Deng, Yuanxin; Shi, Chen Yu; Feringa, Ben L.; Tian, He; Qu, Da Hui

*Published in:*  
Matter

*DOI:*  
[10.1016/j.matt.2021.01.014](https://doi.org/10.1016/j.matt.2021.01.014)

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

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

*Publication date:*  
2021

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

*Citation for published version (APA):*

Zhang, Q., Deng, Y., Shi, C. Y., Feringa, B. L., Tian, H., & Qu, D. H. (2021). Dual closed-loop chemical recycling of synthetic polymers by intrinsically reconfigurable poly(disulfides). *Matter*, 4(4), 1352-1364. <https://doi.org/10.1016/j.matt.2021.01.014>

### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

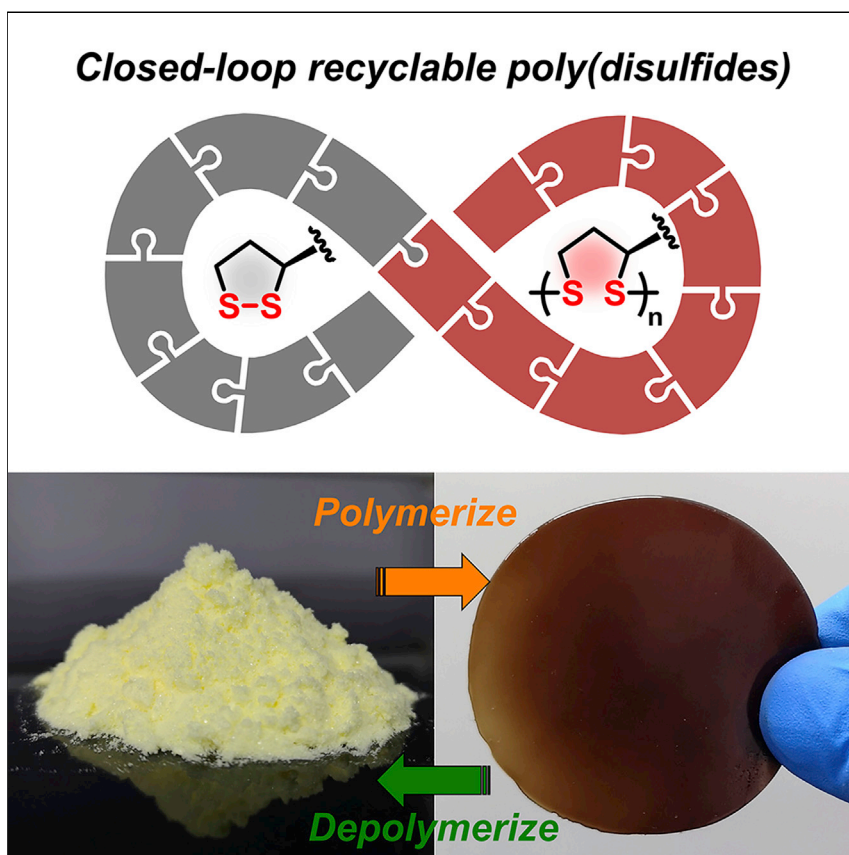
### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

## Article

## Dual closed-loop chemical recycling of synthetic polymers by intrinsically reconfigurable poly(disulfides)



Developing repeatedly recyclable polymers is a timely and urgent task for chemists. An intrinsically reconfigurable polymer made from thioctic acid, a natural small molecule, is found to be a promising candidate for chemically recyclable polymers. Owing to the reversible nature of disulfide bond, the resulting poly(disulfides) can be easily and efficiently recycled by using basic aqueous solution. The reproduced materials exhibit fully recovered properties due to the virgin quality of the recycled monomers, showing the excellent recyclability and great prospects toward future green plastics.

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

b.l.feringa@rug.nl (B.L.F.)  
dahui\_qu@ecust.edu.cn (D.-H.Q.)

**HIGHLIGHTS**

Synthetic poly(disulfides)  
polymers can be chemically  
recycled in a closed loop

The depolymerization process is  
efficiently completed in basic  
aqueous solutions

The chemically recycled materials  
are additive substitutable and  
modulus tunable

**Demonstrate**

Proof-of-concept of performance with  
intended application/response

Zhang et al., Matter 4, 1352–1364  
April 7, 2021 © 2021 Elsevier Inc.  
<https://doi.org/10.1016/j.matt.2021.01.014>



## Article

## Dual closed-loop chemical recycling of synthetic polymers by intrinsically reconfigurable poly(disulfides)

Qi Zhang,<sup>1,2</sup> Yuanxin Deng,<sup>1,2</sup> Chen-Yu Shi,<sup>1</sup> Ben L. Feringa,<sup>1,2,\*</sup> He Tian,<sup>1</sup> and Da-Hui Qu<sup>1,3,\*</sup>

## SUMMARY

The excessive use of plastics has led to severe global problems involving environmental, energy, and health issues and demands for sustainable and recyclable alternatives. Toward 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.

## 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 mean that the current “recyclable” plastics are mostly downcycled 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 feedstocks-products-wastes cycle can be self-sustained in a closed loop.<sup>15</sup> Toward 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

## Progress and potential

It is crucial to develop polymeric materials that can be recycled repeatedly. Here, we show that the intrinsic reconfigurability of poly(thioctic acid) enables the establishment of a closed-loop chemical recycling system among single monomer and two types of polymeric materials. By elaborating the reversible ring-opening polymerization of thioctic acid, both the preparation (polymerization) and recycling (depolymerization) process of this material can be performed in a simple, mild, environmentally friendly, and high-yield manner. The structure and properties of the resulting materials can be easily tuned by the nature of metal ion additives, either exhibiting amorphousness with excellent stretchability and self-healing ability or showing semi-crystallinity with mechanical robustness. This unique polymer combining simplicity of preparation, functional complexity, and chemical recyclability shows great potential in constructing future circular plastic systems.

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 homopolymers avoiding costly, tedious synthesis of monomers. Meanwhile, toward 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 toward elastic self-healing polymers, as well as mechanically robust ionic networks through a cascade of several cycles.

### Preparation and chemical structures 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 TA: (1) low-melting-point TA can be directly transformed into thermoplastic elastomers by one-step solvent-free melting process;<sup>21,23</sup> (2) hydrophobic TA can be transformed into water-soluble sodium salt (TA-Na) after deprotonation by NaOH. The aqueous solution of TA-Na monomers can be directly transformed into a 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 depolymerization, 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 depolymerization 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 is present in traditional open-chain disulfide bonds.<sup>32</sup> This allows TA to readily polymerize under conditions of (1) high concentration to favor intermolecular reactions, and (2) 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 Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Ca<sup>2+</sup>. Thus, amorphous poly(TA) homopolymer instead of co-polymer can be readily prepared by a solvent-free melting method by mixing with specific amounts of metal salts (Figure 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. The homopolymer structure was confirmed by <sup>1</sup>H NMR (Figure S1) and the polymer topology was revealed as

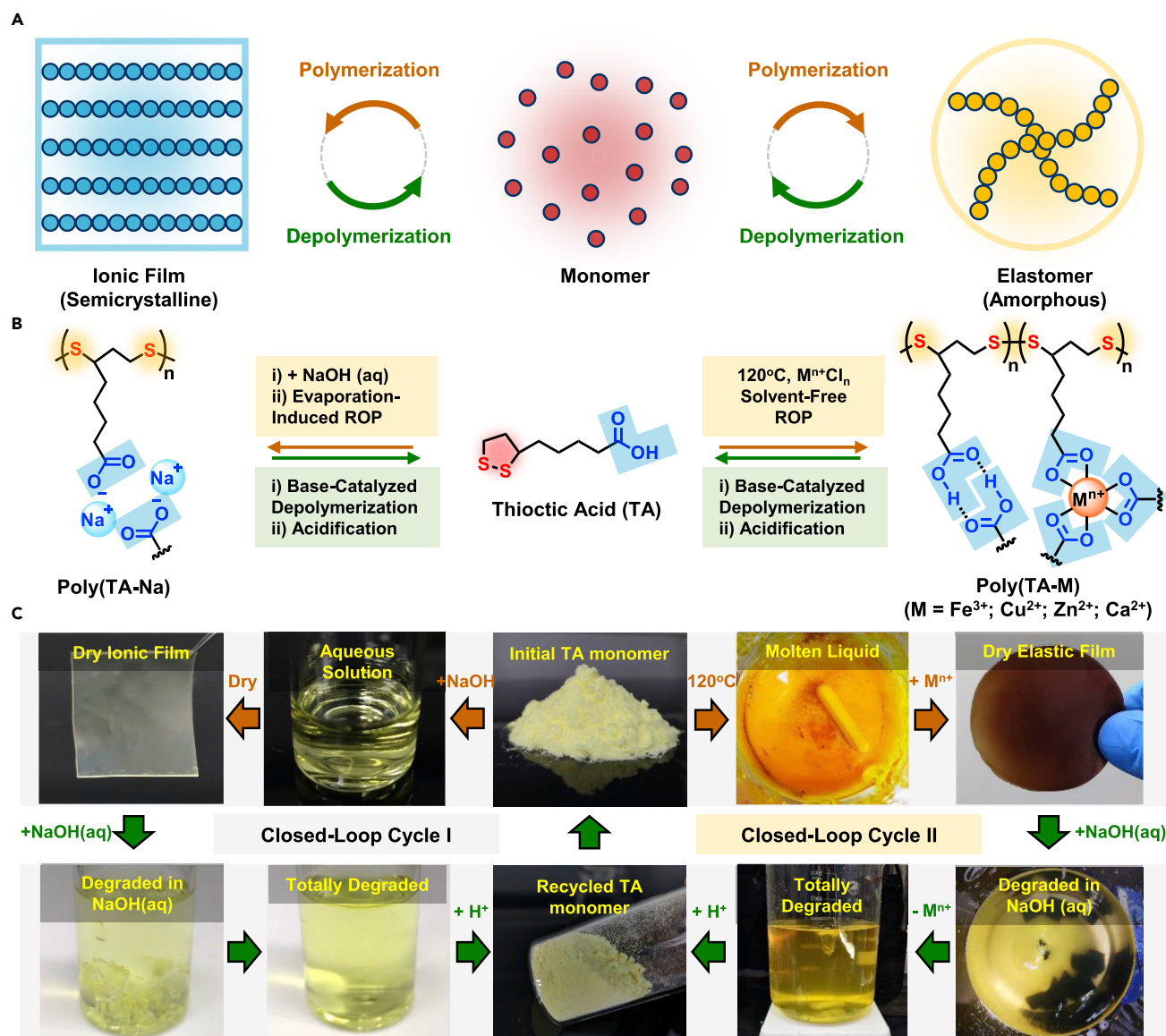
<sup>1</sup>Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, Frontiers Science Center for Materiobiology and Dynamic Chemistry, Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

<sup>2</sup>Stratingh Institute for Chemistry and Zernike Institute for Advanced Materials, Faculty of Science and Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, the Netherlands

<sup>3</sup>Lead contact

\*Correspondence: [b.l.feringa@rug.nl](mailto:b.l.feringa@rug.nl) (B.L.F.), [dahui\\_qu@ecust.edu.cn](mailto:dahui_qu@ecust.edu.cn) (D.-H.Q.)

<https://doi.org/10.1016/j.matt.2021.01.014>



**Figure 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 aqueous 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) ( $M = \text{Fe}^{3+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Ca}^{2+}$ ) film 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.

cyclic polymers by matrix-assisted laser desorption-ionization time of flight mass spectrometry (MALDI-TOF-MS) (Figure S2). The supramolecular network showed insolubility in water and solubility in polar organic solvents (Figure S3). The infrared (IR) spectra of the resulting network showed broad peaks at around  $3,400 \text{ cm}^{-1}$  (Figure S4), which were attributed to the carboxyl groups of TA, but also partially contributed by absorbed  $\text{H}_2\text{O}$  molecules. To eliminate this overlap,  $\text{D}_2\text{O}$  absorbing

experiments were performed. The polymer samples were exposed in D<sub>2</sub>O vapor for 24 h. Then IR spectra of the samples showed the minor presence of D<sub>2</sub>O in the network due to the appearance of broad and low-intensity peaks at 2,000–2,500 cm<sup>-1</sup> (Figure S5), which were attributed to the vibration signal of O–D bonds. Considering the hydrophobic nature of the poly(TA-M) network (according to the insolubility and impermeability of the samples in pure water), we can conclude that minor amounts of water molecules are present in the supramolecular network by forming H-bonds with carboxyl groups. The resulting poly(TA-M) polymers exhibited good mechanical properties (Figure S6), including tunable Young's moduli of 160–660 KPa depending on the nature of the metal ions, as well as excellent stretchability of over 6,000% in all poly(TA-M) samples (Figures S6 and S7). The stretchability was attributed to the existence of an energy dissipation mechanism in the hierarchically assembled supramolecular network (i.e., dynamic nature) containing H-bonds, and metal-carboxylate complexes.<sup>21,23</sup>

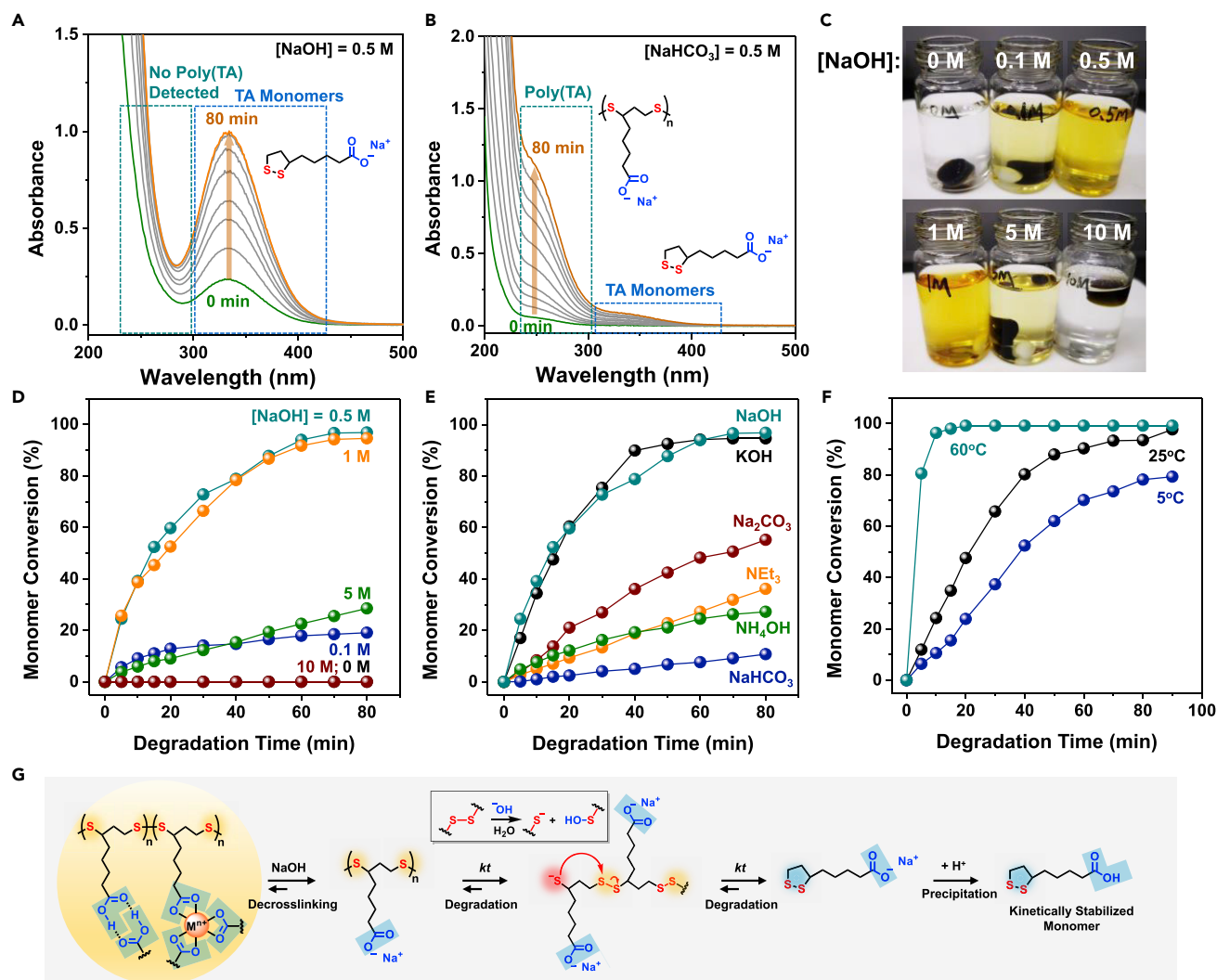
Alternatively, poly(TA-Na) homopolymers can be prepared by the EIISA method,<sup>22</sup> which involves the simple evaporation of an aqueous TA-Na solution at ambient conditions, forming a semi-crystalline layered poly(TA-Na) network crosslinked by ionic bonds (Figure S8). The poly(TA-Na) network exhibited a mechanical robustness at a low relative humidity (<40%), while in preliminary studies we observed softening and elastic behavior after absorbing water and dissolution of the homopolymers in pure water showing partial degradation into monomers and oligomers.<sup>22</sup> The solid film was recovered by evaporating the water again, which is attributed to the reversibility of the dynamic covalent bond, triggering our interest in the possibility of total degradation and chemical recycling of poly(TA-M) homopolymers in aqueous media.

### 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 environmentally friendly nature, we developed a low-cost recycling system to depolymerize poly(TA) polymers in an aqueous alkaline solution.

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 aqueous 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-visible (UV-vis) spectroscopy of the solution (Figure 2A). 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 (Figure 2A). 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) (Figure 2A), 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 peak at around 260 nm attributed to poly(TA), and the low-intensity monomer peak at 330 nm indicated the slower depolymerization (10% conversion after 80 min) catalyzed by weak base NaHCO<sub>3</sub> (Figure 2B). These results revealed that, in alkaline aqueous solution, the crosslinked poly(TA-Fe)





**Figure 2. Base-mediated depolymerization of the poly(TA-Fe) homopolymers**

(A and 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  $\text{NaHCO}_3$  (B). Both of the base concentrations were 0.5 M.

(C and D) Photographs (C) and kinetic curves (D) 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).

(E) Kinetic curves of the monomer conversion percentages in aqueous solution of different bases. All of the base concentrations were 0.5 M.

(F) Temperature-dependent kinetic curves of the monomer conversion percentages of poly(TA-Fe) in 0.5 M aqueous NaOH solution.

(G) Proposed degradation mechanism of the network in an alkaline aqueous solution.

network readily converts into monomers and the base-catalyzed depolymerization process is accelerated by a stronger base.

Furthermore, the depolymerization kinetics of poly(TA-Fe) homopolymers was tested with different concentrations of NaOH (Figures 2C, 2D, and S9). The polymer sample showed no detectable degradation in water in the absence of NaOH. The degradation rate increased with increasing NaOH concentrations (0–0.5 M). In sharp contrast, at concentrations over 0.5 M, the degradation rate showed a remarkably negative correlation with the concentration of NaOH (Figure 2D) and especially no degradation or even any dissolution was observed with 10 M aqueous NaOH. At this high concentration, the polymer sample was found to float in the solution

(Figure 2C). 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 (Figure S10). Furthermore, polymers containing two types of metal ions were also prepared (Figure S11) and the materials showed similar abilities toward depolymerization (Figure S12). Different types of bases were used for depolymerization, revealing that degradation kinetics exhibited a positive correlation with the basicity (Figure 2E). Meanwhile, higher temperatures were found to accelerate the degradation rate of poly(TA-Fe) in aqueous NaOH solution (Figure 2F). 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 (Figure S13), indicating the important role of surface diffusion in this heterogeneous degradation process. The use of  $\text{D}_2\text{O}$  as the solvent was found to make no noticeable difference on the degradation kinetics (Figure S14).

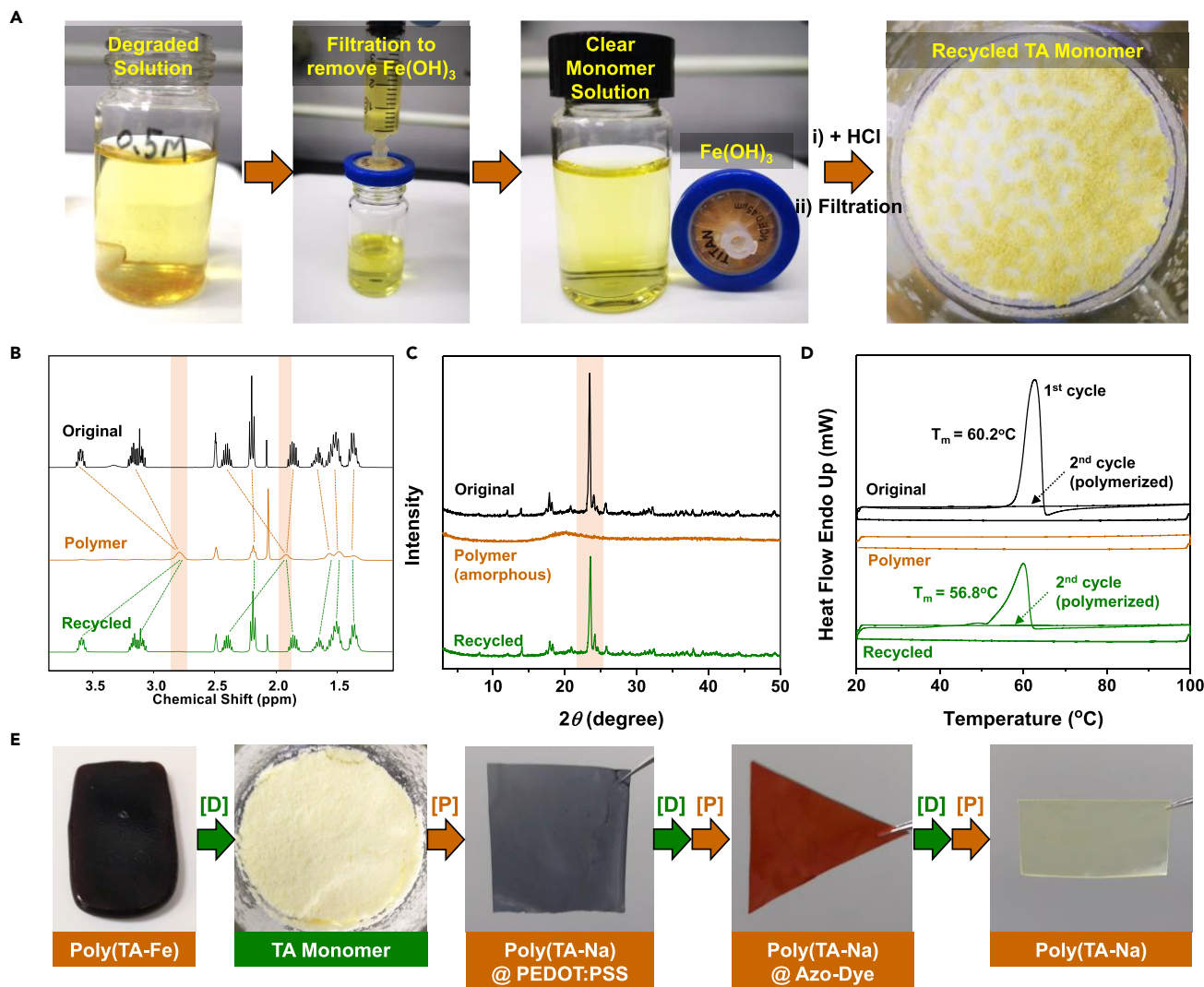
The ionic film of poly(TA-Na) was also depolymerized by the same method but, compared with poly(TA-M) elastomers, the dissolution process of poly(TA-Na) reflects a much faster depolymerization, with complete conversion into TA monomers in 5 min at room temperature (Figure S15). The high degradation rate can be attributed to the fast diffusion of water into the hydrophilic ionic network of poly(TA-Na). As the poly(TA-Na) network showed a low depolymerization rate in neutral water, it allowed real-time detection using UV-vis absorption spectroscopy (Figure S16) and the clear isosbestic point is in accordance with a single conversion process from polymers to monomers.

Based on these findings, a two-step degradation mechanism is proposed (Figure 2G): (1) the hydrogen bonds and iron(III)-carboxylate complexes are “de-cross-linked” 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. (2) Ring-closing depolymerization of poly(TA) homopolymers is catalyzed by the terminal thiolate groups (Figure 2G), which are formed by base-induced disulfide scission.<sup>36</sup> As a consequence, both of poly(TA-M) ( $\text{M} = \text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ) elastomers and the poly(TA-Na) film can be completely degraded into TA monomers by simply stirring the samples in low-concentration aqueous NaOH solutions.

### Chemically recycling of the monomers

The next important step is the separation and purification of TA monomers from the depolymerization 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 (Figure 3A). Then the transparent filtrate containing TA monomers and excess base was acidified ( $\text{pH} = 3\text{--}4$ ) by aqueous hydrochloric acid (1 M) to protonate and precipitate the TA monomers as yellow powders (Figure 3A) in yields of about 60%–80%. The isolation yield presented a negative correlation with the concentrations of TA monomers at the acidification step (Figure S17). The loss of unrecycled TA monomers was attributed to the existence of spontaneous polymerization at the acidification step forming oligomeric colloids, which could not be fully collected by filtration,





**Figure 3. Chemical recycling of the degraded monomers**

(A) Photographs of the facile purification procedure of TA monomers from the degraded mixture.

(B) Partial  $^1\text{H}$  NMR spectra of virgin feedstock, poly(TA-Fe) homopolymers, and 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 Figure S13.

(C and D) Comparison of virgin feedstock, poly(TA-Fe) homopolymers, and recovered monomers by direct acidification method, by XRD (C) and DSC measurements (D).

(E) Photographs of the reproduced polymers in multiple cycles, which allows clean recycling in the presence of metal ions, composite polymers, and dye colorants. [D]/[P] refer to depolymerization/polymerization. The hydrophilic PEDOT:PSS polymers and dyes were removed by repeatedly washing the precipitates with water.

as revealed by (1) the turbid white filtrate after acidification, and (2) the observed polymer/oligomer optical absorption peak at 250 nm of the separated TA solids (Figure S18). The composition of the recycled yellow solids by this method was confirmed as 77% TA monomers containing 23% soluble poly(TA) polymers by analysis of  $^1\text{H}$  NMR spectra (Figure S19).

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 and 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 isolation 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 both of poly(TA-M) elastomers and poly(TA-Na) ionic film. The self-repairing self-assembly mechanism would drive the dynamic system into the same final state<sup>37,38</sup> (i.e., 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 (Figures S20 and S21), revealing the practicality of this recyclable polymer system.

To further confirm the successful recycling of TA monomers, we compared the original feedstock and recycled monomer of TA by <sup>1</sup>H NMR, X-ray diffraction (XRD), Raman spectroscopy, and differential scanning calorimetry (DSC). <sup>1</sup>H NMR spectra showed pure TA monomers obtained by acidification with extraction (Figures 3B and S22), while the recycled TA solids obtained by direct acidification without extraction contained 23% oligomer species (Figure S19). Furthermore, the sharp and consistent diffraction peaks in XRD indicated high crystallinity of the TA monomers recycled by direct acidification (Figure 3C). The Raman spectra (Figure S23) confirmed the successful recycling of TA monomers. Moreover, the DSC curve of TA monomers recycled by direct acidification showed a slightly shifted melting peak at 56.8°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 (Figure 3D). These combined results unequivocally demonstrated the successful chemical recycling of TA monomers from their homopolymers.

The realization of chemical recycling also endowed this polymer system with upcycling ability. A piece of brown thermoplastic poly(TA-Fe) elastomer (5.62 g) was transformed into light yellow TA powders (4.57 g; yield = 82%) by the direct acidification method (Figure 3E). Then the recycled TA powders were dissolved in 20 mL of NaOH aqueous solution (1.1 mM), resulting in a homogeneous yellow solution. Then the yellow monomer solution was mixed with an aqueous solution (5 mL; 1 wt %) poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), a typical conductive polymer,<sup>39</sup> to get a dark blue homogeneous solution, which was then placed into an evaporating dish to allow EISA at ambient condition. After drying overnight, a free-standing polymer film was separated from the disk substrate and the resulting dark blue polymer film exhibited optical translucency (Figure 3E), revealing the good dispersion of PEDOT:PSS colloids in the bulk phase of dry poly(TA-Na) network. To evaluate the recyclability of the resulting poly(TA-Na)@PEDOT:PSS polymer composite, the film sample was degraded by stirring in 0.5 M aqueous NaOH solution, TA recycled by directly acidification, and the hydrophobic PEDOT:PSS readily separated by water washing. Following similar methodology, TA monomers and their polymers can be repeatedly recovered and reproduced in a closed-loop manner (Figure 3E shows multiple cascaded cycles of depolymerization/polymerization), and external additives, such as metal ions, other polymers, and dyes, can be easily separated in the acidification step and the TA monomer isolated and converted into poly(TA-Na) (Figure 3E). As common plastic products are

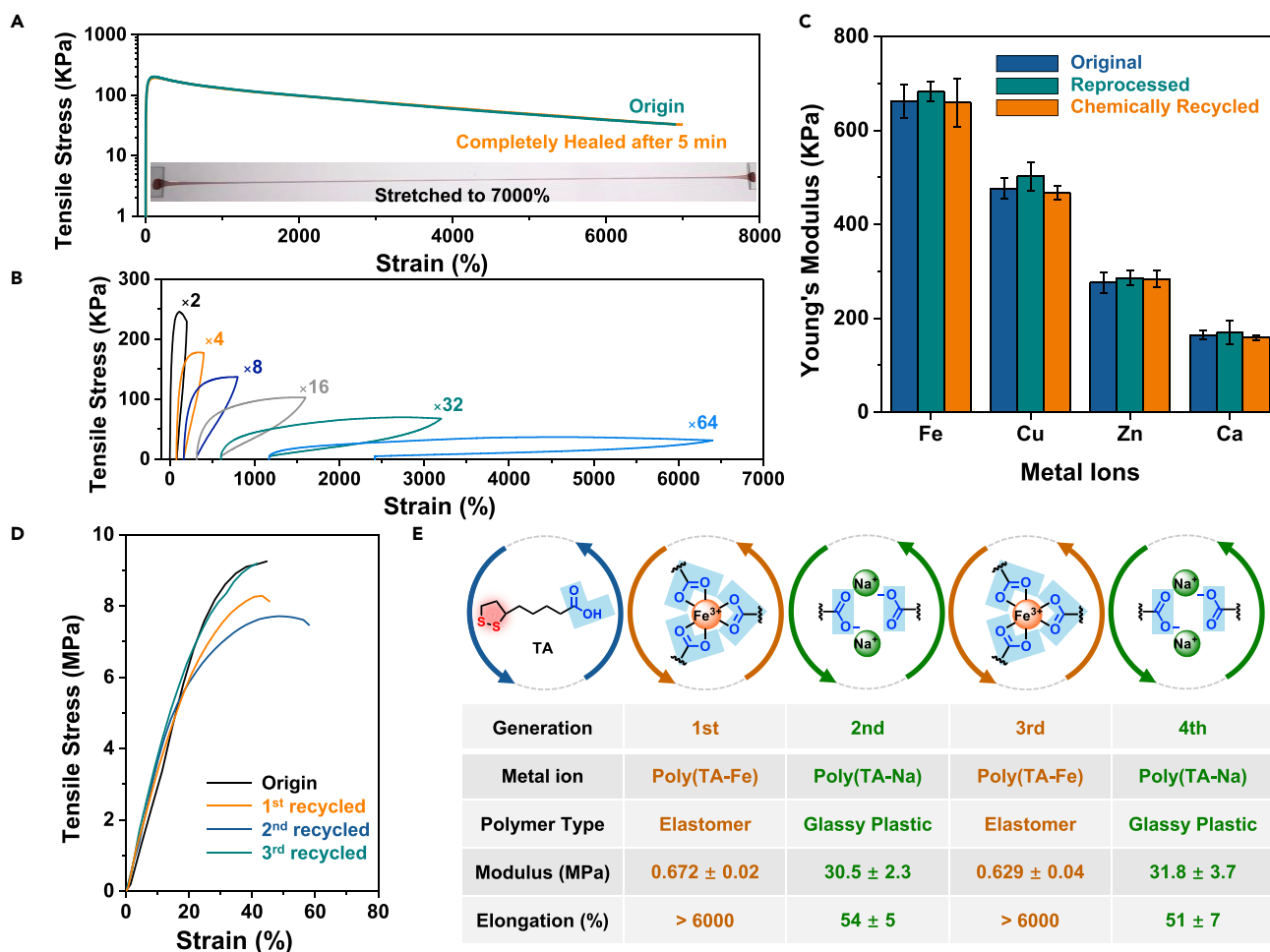
mostly used in the presence of additional additives, this additive-tolerable recyclability is significant for practical applications of plastic recycling systems.<sup>10,37,38</sup>

### 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 downcycled 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 and 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 allowing the material to stand for 5 min under ambient conditions (Figures 4A and S24). The self-healing ability of poly(TA-Fe), including completeness and efficiency, was remarkably increased compared with 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 also endowed the poly(TA-Fe) network with fatigueless mechanical processability. A transparent film could be reformed in 2 h from polymer fragments by simple physical extrusion (about 3 bar) in ambient conditions (Figure S25). The reprocessed polymer membrane showed excellent stretchability in a multi-step cyclic tensile experiment (Figure 4B). Samples after reprocessing still exhibited consistent mechanical performances compared with the virgin material (Figure 4C), suggesting excellent re-processability. Similar self-healing ability and re-processability was also observed in poly(TA-M) (M = Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ca<sup>2+</sup>) networks (Figures 4C and S26), while the mechanically robust poly(TA-Na) ionic network showed no self-healing properties or re-processability due to its limited chain mobility. 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 = Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ca<sup>2+</sup>) elastomers and poly(TA-Na) ionic network] 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 (Figure 4C). Meanwhile, the mechanically robust poly(TA-Na) ionic network also exhibited totally recovered mechanical performance after chemical recycling for three cycles (Figure 4D). 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 small amounts of oligomers present in the recycled feedstock.

Different from mechanical reprocessing, chemical recycling supported external possibilities to reproduce materials with varied chemical composition in every generation of recycling. To experimentally confirm this capability in this polymer system, we performed a total of four generations of cascade recycling experiments, in which the types of every generation of polymers were changed between poly(TA-Fe) elastomers and poly(TA-Na) ionic films (Figure 4E). The excellent mechanical properties



**Figure 4. 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 shows the long filaments stretched to 70 times 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.

(D) Stress-strain curves of poly(TA-Na) network before and after being reformed by chemical recycling method.

(E) Cascaded upcycling experiments between poly(TA-Fe) elastomer and poly(TA-Na) ionic network enabled by chemical recycling method. Error bars show SD with  $n = 3$  repeats.

across generations solidly proved the anti-fatigue ability of chemical recycling method and the important upcycling ability, enabling a cross-recycling loop between different types of polymers from the same feedstock.

## Conclusions

In summary, we have presented a versatile polymer system with closed-loop recyclability, based on the versatile dynamic covalent chemistry of a natural small-molecule TA. Two types of poly(TA) polymers, thermoplastic elastomers and mechanically robust ionic network, 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 and involves a fast depolymerization rate, mild conditions, high-quality recycled monomers, and low cost; is energy-saving and scalable; and 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 toward future high-performance and sustainable materials.

## EXPERIMENTAL PROCEDURES

### Resource availability

#### Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Da-Hui Qu (email: [dahui\\_qu@ecust.edu.cn](mailto:dahui_qu@ecust.edu.cn)).

#### Materials availability

This study did not generate new unique reagents.

#### Data and code availability

This study did not generate/analyze datasets/code.

### 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 to 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 at 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 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.

### Synthesis of Poly(TA-Na) ionic network

The poly(TA-Na) ionic network was prepared according to previous procedures with slight modifications.<sup>22</sup> In a typical experiment, TA powder (2.06 g, 10 mmol) was directly dissolved into aqueous NaOH solution (10 mL, 1 M) by continuous stirring at 80°C, forming a yellow homogeneous solution. The resulting solution was cooled down to room temperature and added to an evaporating dish to evaporate the water at ambient conditions (relative humidity <40%). After completely drying, the robust, semi-crystalline, and transparent film can be separated from the substrate easily, as the poly(TA-Na) ionic network.

### 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 aqueous NaOH solution was used, unless indicated otherwise. The volume of aqueous NaOH solution used was 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 aqueous 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  $\text{Na}_2\text{SO}_4$ , and then mixed with hexane to recrystallize to form virgin-quality TA monomers.

### 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 to 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 or 10 mm/min for poly(TA-Na) ionic network.

### SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.matt.2021.01.014>.

### ACKNOWLEDGMENTS

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.F. acknowledges the financial support of the Netherlands Ministry of Education, Culture and Science (Gravitation program 024.601035). Y.D. 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.

### AUTHOR CONTRIBUTIONS

Q.Z., B.L.F., and D.H.Q. conceived the project and designed the experiments. Q.Z., Y.D., and C.Y.S. performed the experiments, characterized the materials, and analyzed the data under the supervision of D.H.Q. The draft was written by Q.Z. and revised by Q.Z., D.H.Q., B.L.F., and H.T. All authors participated in the discussion and revision of the manuscript.

### DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: November 13, 2020

Revised: December 18, 2020

Accepted: January 11, 2021

Published: February 4, 2021



## REFERENCES

- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., and Law, K.L. (2015). Plastic waste inputs from land into the ocean. *Science* 347, 768–771.
- Zhu, Y., Romain, C., and Williams, C.K. (2016). Sustainable polymers from renewable resources. *Nature* 540, 354–362.
- Schneiderman, D.K., and Hillmyer, M.A. (2017). 50th anniversary perspective: there is a great future in sustainable polymers. *Macromolecules* 50, 3733–3749.
- Sardon, H., and Dove, A.P. (2018). Plastics recycling with a difference. *Science* 360, 380–381.
- Rahimi, A., and García, J.M. (2017). Chemical recycling of waste plastics for new materials production. *Nat. Rev. Chem.* 1, 0046.
- Science to enable sustainable plastics. (2020) A white paper from the 8th Chemical Sciences and Society Summit (CS3), London, UK.
- Tullo, A.H. (2019). Plastic has a problem; is chemistry the solution? *Chem. Eng. News* 97, 29–34.
- Maris, J., Bourdon, S., Brossard, J.M., Cauret, L., Fontaine, L., and Montembault, V. (2018). Mechanical recycling: compatibilization of mixed thermoplastic wastes. *Polym. Degrad. Stabil.* 147, 245–266.
- Zhu, J.B., Watson, E.M., Tang, J., and Chen, E.Y.X. (2018). A synthetic polymer system with repeatable chemical recyclability. *Science* 360, 398–403.
- Zhang, X., Fevre, M., Jones, G.O., and Waymouth, R.M. (2018). Catalysis as an enabling science for sustainable polymers. *Chem. Rev.* 118, 839–885.
- Westhues, S., Idel, J., and Klankermayer, J. (2018). Molecular catalyst systems as key enablers for tailored polyesters and polycarbonate recycling concepts. *Sci. Adv.* 4, eaat9669.
- Christensen, P.R., Scheuermann, A.M., Loeffler, K.E., and Helms, B.A. (2019). Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds. *Nat. Chem.* 11, 442–448.
- Xu, Z., Liang, Y., Ma, X., Chen, S., Yu, C., Wang, Y., Zhang, D., and Miao, M. (2020). Recyclable thermoset hyperbranched polymers containing reversible hexahydro-s-triazine. *Nat. Sustain.* 3, 29–34.
- Zou, Z., Zhu, C., Li, Y., Lei, X., Zhang, W., and Xiao, J. (2018). Rehealable, fully recyclable, and malleable electronic skin enabled by dynamic covalent thermoset nanocomposite. *Sci. Adv.* 4, eaq0508.
- Aida, T., and Meijer, E.W. (2020). Supramolecular polymers—we've come full circle. *Isr. J. Chem.* 60, 33–47.
- Jehanno, C., and Sardon, H. (2019). A step towards truly recyclable plastics. *Nature* 568, 467–468.
- Yuan, J., Xiong, W., Zhou, X., Zhang, Y., Shi, D., Li, Z., and Lu, H. (2019). 4-Hydroxyproline-derived sustainable polythioesters: controlled ring-opening polymerization, complete recyclability, and facile functionalization. *J. Am. Chem. Soc.* 141, 4928–4935.
- Jing, B.B., and Evans, C.M. (2019). Catalyst-free dynamic networks for recyclable, self-healing solid polymer electrolytes. *J. Am. Chem. Soc.* 141, 18932–18937.
- Lloyd, E.M., Lopez Hernandez, H., Feinberg, A.M., Yourdkhani, M., Zen, E.K., Mejia, E.B., Sottos, N.R., Moore, J.S., and White, S.R. (2018). Fully recyclable metastable polymers and composites. *Chem. Mater.* 31, 398–406.
- Zimmerman, J.B., Anastas, P.T., Erythropel, H.C., and Leitner, W. (2020). Designing for a green chemistry future. *Science* 367, 397–400.
- Zhang, Q., Shi, C.Y., Qu, D.H., Long, Y.T., Feringa, B.L., and Tian, H. (2018). Exploring a naturally tailored small molecule for stretchable, self-healing, and adhesive supramolecular polymers. *Sci. Adv.* 4, eaat8192.
- Zhang, Q., Deng, Y.X., Luo, H.X., Shi, C.Y., Geise, G.M., Feringa, B.L., Tian, H., and Qu, D.H. (2019). Assembling a natural small molecule into a supramolecular network with high structural order and dynamic functions. *J. Am. Chem. Soc.* 141, 12804–12814.
- Deng, Y., Zhang, Q., Feringa, B.L., Tian, H., and Qu, D.H. (2020). Toughening a self-healable supramolecular polymer by ionic cluster-enhanced iron-carboxylate complexes. *Angew. Chem. Int. Ed.* 59, 5278–5283.
- Black, S.P., Sanders, J.K., and Stefankiewicz, A.R. (2014). Disulfide exchange: exposing supramolecular reactivity through dynamic covalent chemistry. *Chem. Soc. Rev.* 43, 1861–1872.
- Houk, J., and Whitesides, G.M. (1987). Structure-reactivity relations for thiol-disulfide interchange. *J. Am. Chem. Soc.* 109, 6825–6836.
- Singh, R., and Whitesides, G.M. (1990). Degenerate intermolecular thiolate-disulfide interchange involving cyclic five-membered disulfides is faster by approx.  $10^3$  than that involving six- or seven-membered disulfides. *J. Am. Chem. Soc.* 112, 6304–6309.
- Bang, E.K., Gasparini, G., Molinard, G., Roux, A., Sakai, N., and Matile, S. (2013). Substrate-initiated synthesis of cell-penetrating poly(disulfide)s. *J. Am. Chem. Soc.* 135, 2088–2091.
- Zhang, X., and Waymouth, R.M. (2017). 1,2-dithiolane-derived dynamic, covalent materials: cooperative self-assembly and reversible cross-linking. *J. Am. Chem. Soc.* 139, 3822–3833.
- Pulcu, G.S., Galenkamp, N.S., Qing, Y., Gasparini, G., Mikhailova, E., Matile, S., and Bayley, H. (2019). Single-molecule kinetics of growth and degradation of cell-penetrating poly(disulfide)s. *J. Am. Chem. Soc.* 141, 12444–12447.
- Liu, Y., Jia, Y., Wu, Q., and Moore, J.S. (2019). Architecture-controlled ring-opening polymerization for dynamic covalent poly(disulfide)s. *J. Am. Chem. Soc.* 141, 17075–17080.
- Lu, J., Wang, H., Tian, Z., Hou, Y., and Lu, H. (2020). Cryopolymerization of 1,2-dithiolanes for the facile and reversible grafting-from synthesis of protein-polydisulfide conjugates. *J. Am. Chem. Soc.* 142, 1217–1221.
- Bartrop, J.A., Hayes, P.M., and Calvin, M. (1954). The chemistry of 1,2-dithiolane (trimethylene disulfide) as a model for the primary quantum conversion act in photosynthesis. *J. Am. Chem. Soc.* 76, 4348–4367.
- Thomas, R.C., and Reed, L.J. (1956). Disulfide polymers of DL- $\alpha$ -lipoic acid. *J. Am. Chem. Soc.* 78, 6148–6149.
- Endo, K., and Yamanaka, T. (2006). Copolymerization of lipoic acid with 1,2-dithiane and characterization of the copolymer as an interlocked cyclic polymer. *Macromolecules* 39, 4038–4043.
- Scheutz, G.M., Rowell, J.L., Ellison, S.T., Garrison, J.B., Angelini, T.E., and Sumerlin, B.S. (2020). Harnessing strained disulfides for photocurable adaptable hydrogels. *Macromolecules* 53, 4028.
- Parker, A.J., and Kharasch, N. (1959). The scission of the sulfur-sulfur bond. *Chem. Rev.* 59, 583–628.
- Bang, E.K., Lista, M., Sforzazzini, G., Sakai, N., and Matile, S. (2012). Poly(disulfide)s. *Chem. Sci.* 3, 1752–1763.
- Wilson, A., Gasparini, G., and Matile, S. (2014). Functional systems with orthogonal dynamic covalent bonds. *Chem. Soc. Rev.* 43, 1948–1962.
- Wang, Y., Zhu, C., Pfattner, R., Yan, H., Jin, L., Chen, S., Molina-Lopez, F., Lissel, F., Liu, J., Rabiah, N.I., et al. (2017). A highly stretchable, transparent, and conductive polymer. *Sci. Adv.* 3, e1602076.
- Liu, K., Jiang, Y., Bao, Z., and Yan, X. (2019). Skin-inspired electronics enabled by supramolecular polymeric materials. *CCS Chem.* 1, 431–447.
- Lee, H.R., Kim, C.C., and Sun, J.Y. (2018). Stretchable ionics—a promising candidate for upcoming wearable devices. *Adv. Mater.* 30, 1704403.
- Garcia, J.M., and Robertson, M.L. (2017). The future of plastics recycling. *Science* 358, 870–872.