

# Modulating Metallopolymer Mechanical Properties by Controlling Metal Ligand Crosslinking

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**INTRODUCTION** Noncovalent interactions such as hydrogen bonds, hydrophobic interaction, and metal–ligand interactions (neutral and ionic) enable networks in both natural systems<sup>1,2</sup> and synthetic materials.<sup>3–6</sup> These noncovalent networks can potentially mimic classical covalent network behaviors such as elastic recovery from large deformation and swelling in the presence of good solvents,<sup>7,8</sup> while boasting appealing properties such as self-healing,<sup>9,10</sup> processability,<sup>11,12</sup> energy absorption,<sup>13</sup> self-assembly,<sup>14</sup> and stimuli responsiveness.<sup>15,16</sup> This combination of covalent-like and dynamic properties is accomplished by tuning the dynamics of the network connections. Metallopolymers in particular have attracted much attention in the past two decades due to their possible mechanical properties, synthetic methodologies, and processing.<sup>17,18</sup> Metallopolymers are highly customizable since in addition to normal polymer control knobs such as monomer selection, molecular weight and architecture, metallopolymers can be differentiated by where the metal complexes are bound in the polymer architecture (i.e., as crosslinkers, side chain substituent, or part of a linear backbone), and by the type of metal cation and ligand chemistry.<sup>17</sup>

The strength of the metal complex to resist breaking under mechanical force has been shown to strongly influence the mechanical behavior of metallopolymers.<sup>19–21</sup> It was demonstrated that by clever design of supramolecular polymers, metallopolymers synthesized with different metals<sup>19,20,22</sup> or different ligands<sup>21,23</sup> presented diverse organometallic interactions that lead to different stiffness, toughness, and viscoelastic dissipation. These distinct mechanical behaviors can also be controlled by external stimuli. The groups of Holten–Andersen and Meyer showed how changing metal–ligand interactions in metallo-hydrogels by changing the pH,<sup>8</sup> the oxidation state of the metals with UV exposure,<sup>24</sup> or

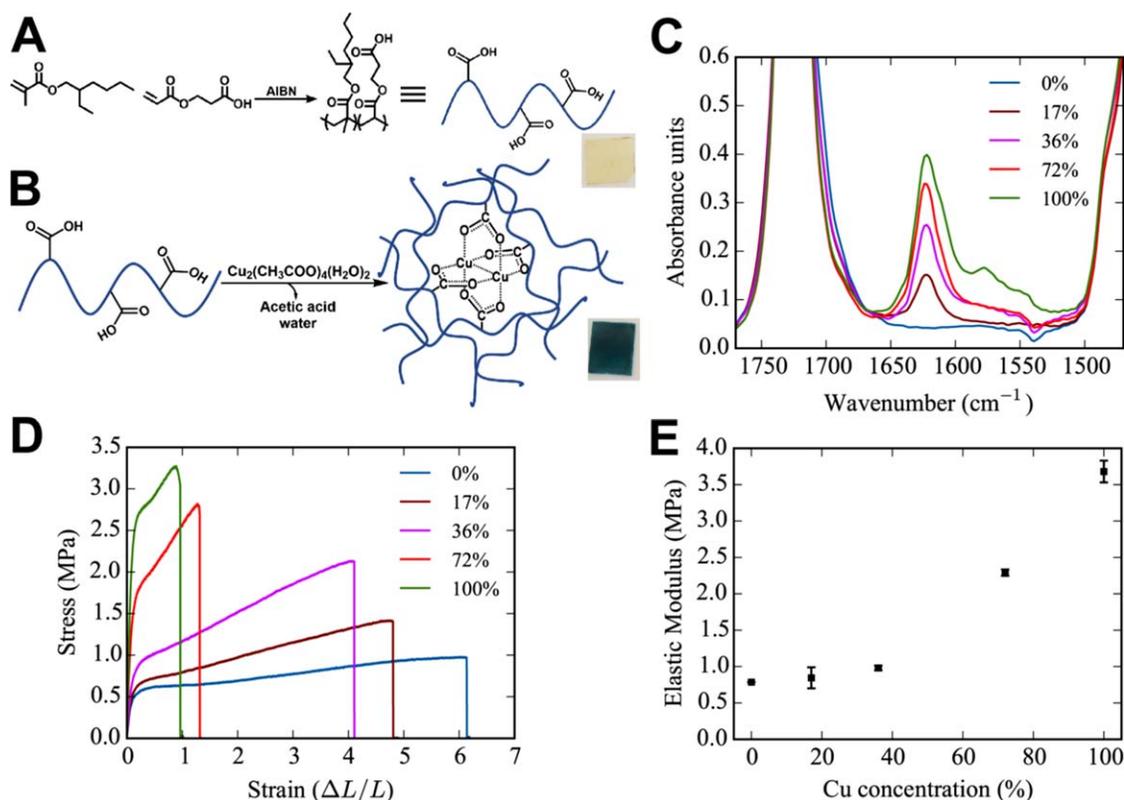
electrochemically<sup>25,26</sup> allowed control over mechanical properties. Recently, Manners et al. showed that polarity and coordination ability of a solvent dictate the dynamic nature of metal–ligand interactions in a poly-nickelocene solution.<sup>27</sup>

Here we present an innovative material system in which the addition of copper(II) to a linear elastomer increases strength and decreases ductility through the formation of metal–ligand bonds that behave in a covalent-like manner. Unlike covalent crosslinks, however, the copper-based crosslinks can be weakened and even removed with proper choice of ligands, enabling full thermoplastic-like processing. Furthermore, we show in our final portion that ligands can be incorporated within the solid-state material, essentially removing or making the crosslinks mechanically dynamic, increasing toughness, and enabling self-healing. In contrast to much of the previous work in this field, our polymers are solid even without the metal–ligand bonds, making the dynamic behavior regime, and its applications distinct.

Our design strategy for creating an elastomer with crosslinking controlled by metal ion content was the random copolymerization of 2-ethylhexyl methacrylate together with 2-carboxyethyl acrylate [Fig. 1(a)]. The ethylhexyl acrylic backbone makes a highly stretchable material and the dangling carboxylic acid side groups are potential sites for crosslinking by divalent cations.<sup>28</sup> The percentage of carboxylic acid on the linear polymer was 15% as determined by proton NMR (Supporting Information, Figs. S1 and S2). We selected copper(II) cations to react with the grafted carboxylic side groups on the polymer backbone to generate the noncovalent crosslinking system [Fig. 1(b)]. The polymer can be easily crosslinked when exposed to copper(II) acetate mono hydrate due to the fast ligand exchange of the anionic ligands (Supporting Information, Movie 1). To verify that the crosslinking of the polymeric network is through copper

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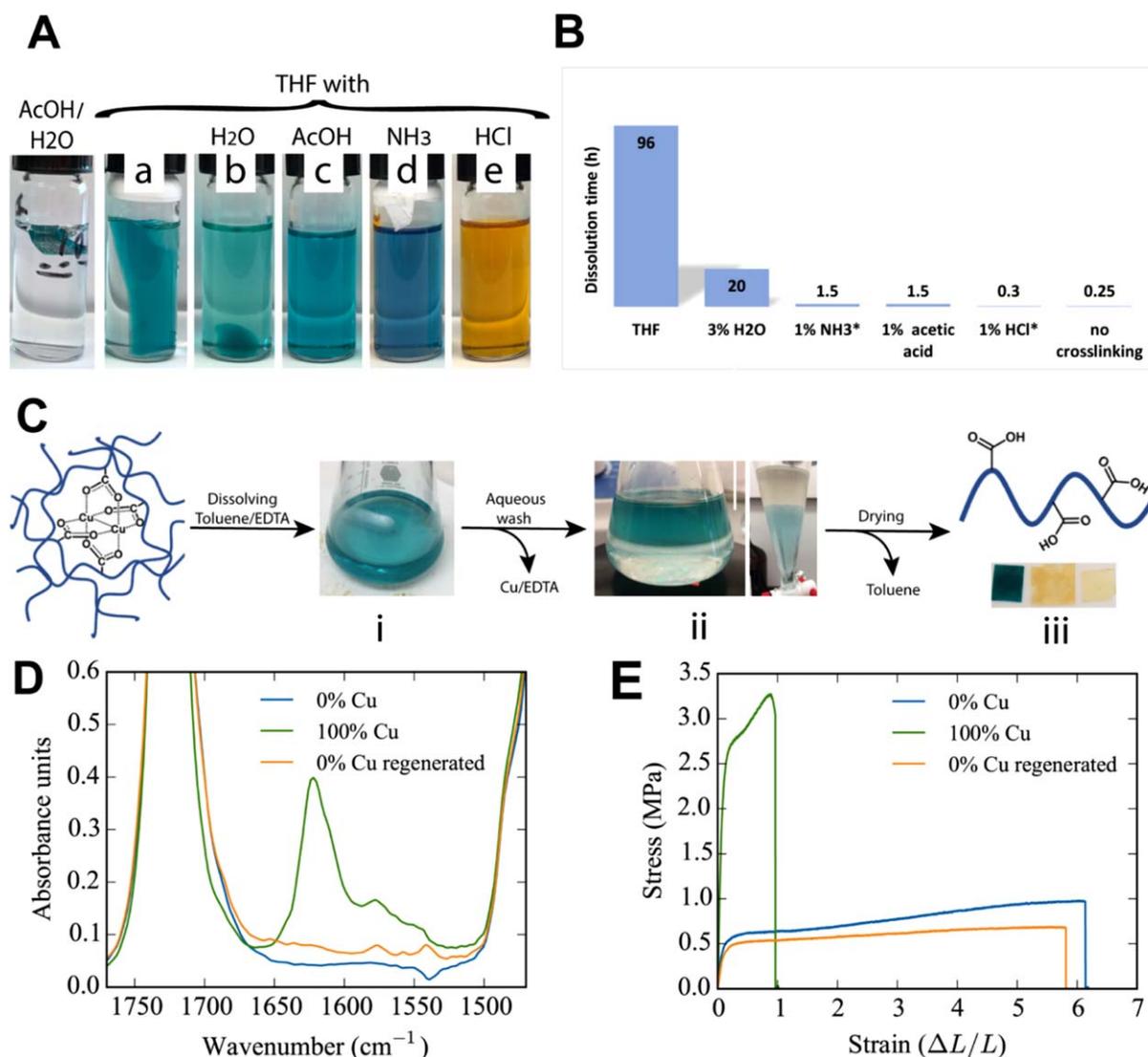
**FIGURE 1** (A) Synthesis of the linear copolymer ethylhexyl methacrylate grafted with carboxylic acid side groups (PEC) and its appearance after molding (rectangle, bottom right). (B) Crosslinking of PEC with copper(II) acetate mono hydrate and its appearance after molding (rectangle, bottom right). (C) IR spectrum of PEC with increasing amounts of copper(II) at the carbonyl stretching absorption range. (D) Stress–strain curves of PEC with different amounts of copper(II). (E) Elastic modulus of PEC with increasing amounts of copper(II). [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

carboxylate, we synthesized a model system based on the replacement of the acetate anions in copper(II) acetate by less volatile laurate anions at the same condition as the crosslinking reaction (Supporting Information, Fig. S3). NMR of copper(II) acetate with excess of lauric acid in  $\text{CDCl}_3$  shows broadening and shift of the peaks assigned to lauric acid, indicating fast equilibrium between the different ionic species (Supporting Information, Fig. S4). Electrospray ionization mass spectrometry (ESI-MS) analysis shows that under crosslinking conditions all acetate anions were replaced to obtain the copper(II) laurate complex (Supporting Information, Fig. S5). In the co-polymers, copper(II) carboxylate forms a dimer structure containing two copper(II) cations attached by four different carboxylate anions [Fig. 1(b)].<sup>29</sup> This tetra-functional ionic interaction will behave in a covalent manner over laboratory time frames as discussed in the following sections. As a control, we processed the homopolymer poly(2-ethylhexyl methacrylate) with copper(II) acetate in the same crosslinking conditions like the carboxylic acid co-polymers (Supporting Information, Fig. S6).

Copper(II)-crosslinked copolymers were created with copper ion content varying from 0% of the potential sites (PEC-Cu0) to 100% of the potential sites (PEC-Cu100), corresponding to 0%–15% crosslinking. The copper-containing copolymer

has a homogeneous green–blue appearance. The percent of occupied sites was determined from the shift in the carbonyl peak to 1624  $\text{cm}^{-1}$  in the IR spectrum [Fig. 1(c)]. The control homopolymer processed with copper(II) acetate had a swirled greenish–brown appearance (Supporting Information, Fig. S6). The IR spectrum of this control polymer did not show any changes compared to the homopolymer without copper (Supporting Information, Fig. S7).

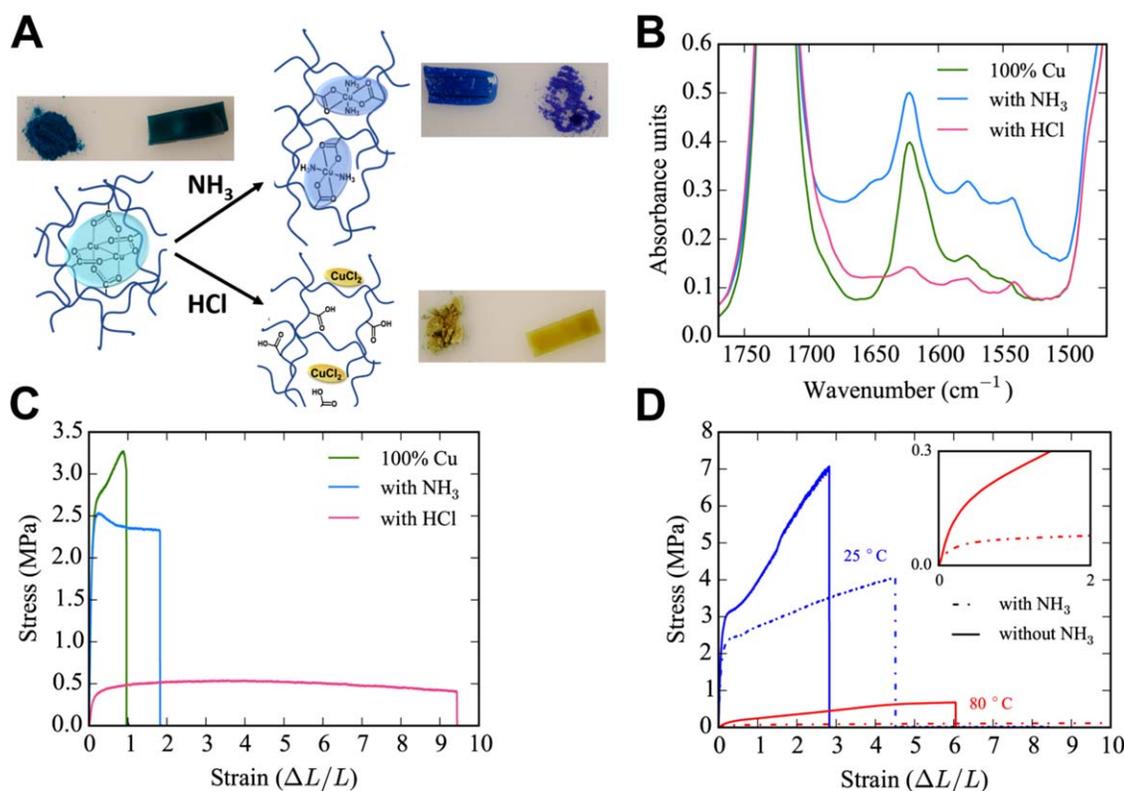
The mechanical properties of the obtained polymers depend strongly on the quantity of added copper [Fig. 1(d)]. All materials were tested under quasi-static monotonic tension at 25 °C. The base linear polymer is a highly ductile material with an elastic modulus of 7.9 MPa, flow stress of 0.62 MPa, and failure strain of 6.5. The higher the percentage of copper crosslinking, the higher the stiffness and strength and lower the ductility. When copper is increased to 100% of potential sites (PEC-Cu100), the elastic modulus is 37 MPa, flow stress is 2.7 MPa, and failure strain is 0.84. The trends in flow stress and failure strain are monotonic. The elastic modulus is relatively flat for low crosslinking and then increases drastically above 40% [Fig. 1(e)] suggesting significant topological changes. The control homopolymer shows no change in mechanical properties compared to the version without copper (Supporting Information, Fig. S8).



**FIGURE 2** (A) PEC-Cu100 after 2 h in THF with different ligands: (a) no additives, (b) 3% water, (c) 1% acetic acid, (d) 1% NH<sub>3</sub>, and (e) 1% HCl. (B) Dissolution times of 100mg PEC-Cu100 in 3 mL of THF with different ligands. \*NH<sub>3</sub> and HCl were added as saturated solutions in water. (C) Scheme of the linear polymer regeneration process: (i) dissolution of the copper(II) crosslinked polymer by the addition of EDTA; (ii) extraction of the copper ions from the upper polymer/toluene phase to the lower aqueous phase; (iii) on the bottom: PEC-Cu100 (left), regenerated PEC-Cu0 (middle), original PEC-Cu0 (right). (D) IR spectrum at the carbonyl stretching absorption of virgin PEC-Cu0, copper crosslinked PEC-Cu100, and regenerated PEC-Cu0. (E) Stress–strain curves of virgin PEC-Cu0, copper crosslinked PEC-Cu100, and regenerated PEC-Cu0. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

A key advantage of the metal–ligand crosslinking bonds is that the choice of solution medium can control whether the bonds act in a covalent manner.<sup>27</sup> The copper(II) carboxylate ionic interaction is similar to a covalent crosslinker in the presence of good solvents that easily dissolve the linear polymer. Immersing the 100% Cu(II)-crosslinked polymer (PEC-Cu100) in a hydrophobic solvent such as toluene, which serves as excellent solvent for the linear polymer, did not cause dissolution of the polymer or change in the solvent color even after one week. While the more crosslinked PEC-Cu100 almost did not change its original dimensions, the less crosslinked PEC-Cu72 swelled by 500% after 24 h. Immersion in a more polar and coordinating solvent (THF)

caused swelling of PEC-Cu100 by 400% and complete dissolution after 96 h. Addition of ligands, neutral, or anionic, resulted in a dramatic reduction of dissolution time of the polymer [Fig. 2(a,b) and Supporting Information, Movie 2]. The color changes generated by the addition of ammonia and hydrochloric acid to the polymeric solutions are similar to the changes that occur with the pure copper(II) acetate salt and consistent with the generation of Cu(CH<sub>3</sub>COO)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub><sup>30</sup> and CuCl<sub>2</sub> respectively.<sup>31</sup> The reduction in dissolution time can be explained by the weakening or complete detachment of copper carboxylate interactions due to the attachment of different ligands to the copper cation.



**FIGURE 3** (A) Changes in the crosslinking nature and color caused by the addition of HCl and  $\text{NH}_3$  ligands to the copper(II) cross-linked polymer. (B) The carbonyl stretching absorption of PEC-Cu100 before and after reaction with  $\text{NH}_3$  and HCl. (C) Stress-strain curves of PEC-Cu100 before and after reaction with  $\text{NH}_3$  and HCl. (D) Stress-strain curves of PEC'-Cu70 with  $\text{NH}_3$  and without  $\text{NH}_3$  at room temperature and 80 °C. Inset: zoomed in view of data at 80 °C. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

The ability to easily dissolve the metal-ligand crosslinked polymer was used to regenerate the original linear polymer [Fig. 2(c,e)]. Figure 2(c) illustrates the regeneration process (see details in Supporting Information). The copper ions were extracted from the toluene-swollen polymer through the addition of a strong, water soluble, ligand (EDTA) that attaches to the copper. The ligand-copper complex can then be separated by an aqueous wash, leaving a separate phase of linear co-polymer in toluene. The shift of the copper(II) ions from the polymer phase to the water phase is apparent from their distinct blue color [Fig. 2(c)]. The regenerated linear polymer presents the same appearance, IR, and NMR spectra as the original linear polymer [Fig. 2(c,d) and Supporting Information, Fig. S9], and the same mechanical behavior under tensile testing [Fig. 2(e)].

Based on the striking impact of ligands on the polymer solubility and color, we hypothesized that the addition of ligands to the solid-state polymer would modulate mechanical properties by eliminating or making the crosslinks more dynamic. The ammonia-modified polymer was prepared by reacting the copper(II) carboxylate crosslinked copolymer with ammonia (Supporting Information). Copper(II) acetate coordinated with ammonia ligands were synthesized by adding concentrated ammonia to copper acetate as indicated by the dark blue-purple color and confirmed by single crystal X-ray

diffraction (Supporting Information). The addition of ammonia ligands to the copper complex breaks the dimeric structure, generating twice the number of crosslinking sites [Fig. 3(a)]. The presence of the peak at 1624  $\text{cm}^{-1}$  at the IR spectrum of the ammonia-modified polymer [Fig. 3(b)] confirms the attachment of copper(II) and carboxylate. The crystal structure reveals that the attachment of ammonia changes the bond distances between the carboxylate oxygens and copper from 1.935 to 2.005 Å for the four bonds to two distinct distances of 2.005 Å and 2.680 Å.<sup>29,30</sup> The difference in bond distance in the ammonia complex indicates that the copper cation is bound to each carboxylate only through one strong ionic interaction with the second oxygen only weakly coordinated to the copper cation. The crosslinked polymer with ammonia ligands exhibits similar stiffness, higher stretchability, and slightly lower strength than the ammonia-free polymer with the same quantity of copper [Fig. 3(c)]. To understand whether these changes in mechanical behavior are dominated by the difference in network topology of the tetrafunctional versus difunctional complex or are the result of the more dynamic nature of the ammonia-modified bond, both copper crosslinked and the ammonia-modified materials were tested at elevated temperature (80 °C) and different strain rates (0.001–0.1  $\text{s}^{-1}$ ). These experiments were conducted on a different batch of materials with lower loading of carboxylic acid PEC'-Cu0 (Supporting Information, Fig.

S10a). At room temperature both materials exhibit a moderate strain rate dependence (Supporting Information, Fig. S10b), as expected from the combination of entanglements and cross-links governing the mechanical behavior of the polymers. For all rates, the ammonia-modified material has less strain hardening and greater ductility. At 80 °C where the polymer itself has mobility, the ammonia-modified material flows much more easily than the ammonia-free [Fig. 3(d)]. The ratio of their flow stresses doubles from 1.3 to 2.6 suggesting that the differences in mechanical behavior are dominated by the dynamic nature of the ammonia-modified bond.

Separately, the copper(II) carboxylate copolymer was reacted with hydrochloric acid. Reacting copper(II) carboxylate with hydrochloric acid causes the carboxylate to detach from the copper cation and generate copper chloride salt and free carboxylic acid [Fig. 3(a)]. This reaction caused the same color change from blue to yellow as in solution, indicating that the copper cation generated copper chloride salt. The resulting yellow polymer did not show the carboxylate carbonyl peak at  $1624\text{ cm}^{-1}$  at the IR spectrum [Fig. 3(b)]. The hydrochloric acid modified polymer exhibited mechanical behavior similar to the linear polymer, as expected from the generation of salt instead of crosslinks [Fig. 3(c)].

The self-healing performance of the metallo-crosslinked polymers was also characterized to probe the dynamic nature of the crosslinking. As even the linear polymer does not show self-healing behavior in reasonable time scales at room temperature, self-healing was conducted at an elevated temperature. The copper(II) crosslinked polymer PEC-Cu100 did not show any ability to self-heal even at 140 °C, supporting the covalent-like nature of copper(II) carboxylate (Supporting Information, Movie 3). This same material modified by ammonia demonstrated self-healing capability at 80 °C (Supporting Information, Movies 4 and 5), further supporting the dynamic nature of the ammonia-modified crosslinking bonds.

In this article, we demonstrated that by changing the dynamic nature of metal-ligand crosslinking, we were able to control the mechanical, solubility, and self-healing properties of metal containing elastomers. The addition of copper(II) acetate to carboxylic acid grafted poly-(ethylhexyl methacrylate) generated copper(II) carboxylate crosslinking that acts covalently and can be used to control the effective degree of crosslinking. The covalent-like nature of the crosslinking is apparent both in the mechanical response and in the swelling behavior. Attachment of different ligands to the copper cation made the copper carboxylate bond more dynamic, resulting in dramatic reduction of dissolution times in solution and greater ductility in solid-state mechanical testing. This ligand modulation of the crosslinking was used to remove the copper cations from the polymer to regenerate the initial linear polymer. The ligand modulation was also used to enable self-healing. The scheme of polymer property control presented here is adaptable to many different metal ions and polymer backbones, making the range of accessible mechanical properties vast.

## EXPERIMENTAL SECTION

### Polymer Synthesis

2-ethylhexylmethacrylate (100 mL, 450 mmol) and 2-carboxyethyl acrylate (7.15 g, 50 mmol) were stirred in 500 mL toluene. Nitrogen was bubbled through the resulting solution for 30 min. The reaction was set at 65 °C and azobisisobutyronitrile (407 mg, 2.5 mmol) dissolved in 5 mL of toluene was added dropwise, and the reaction proceeded for 12 h. Polymer purification involved precipitation of the reaction mixture in excess of methanol three times followed by drying in a vacuum oven for 48 h at 140 °C to obtain 71 g (yield 71%). The final product was a transparent elastomeric solid. Chemical structures and amount of carboxylic acid were determined using NMR (Bruker 500) and ATR-FTIR (Supporting Information).

### Crosslinking

$\text{Cu}_2(\text{AcO})_2 \cdot (\text{H}_2\text{O})_2$  in THF/ethanol/AcOH (2/5/0.2 mL) was added to 3.0 g of the linear co-polymer dissolved in toluene (10 mL). The mixture was transferred to a silicone mold and the solvents were evaporated slowly and then dried at 140 °C under vacuum.

### Mechanical Properties

Rectangular tensile specimens 5 mm wide were cut with a razor-blade from the solvent evaporated polymer that is  $\sim 1$  mm thick. These specimens were tested under displacement control within a Zwick/Roell Z010, at 25 °C, with gage length set to 20 mm. The crosshead displacement rate was set to  $0.2\text{ mm s}^{-1}$ , corresponding to an engineering strain rate of  $0.01\text{ s}^{-1}$ . Engineering stress was calculated by dividing force by the initial area.

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