Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

Bridging experiments and theory: isolating the effects of metal-ligand interactions on viscoelasticity of reversible polymer networks

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S1. Materials and methods.

Materials. Lauryl methacrylate (LMA), (2-acetoacetoxy)ethyl methacrylate (AAEMA), 2,2′-azobis(2-methylpropionitrile) (AIBN), 2-cyano-2-propyl benzodithioate, ethyl acetate, N,N-dimethylformamide (DMF), chloroform, hexane, copper(II) acetate hydrate and nickel(II) acetate tetrahydrate were purchased from Millipore Sigma. Aluminum oxide (Al_2O_3, activated, basic) and zinc acetate were purchased from Alfa Aesar. Methanol was purchased from Macron Fine Chemicals. Anisole was purchased from Oakwood Chemicals. All solvents were ACS grade. Materials were used as received, unless otherwise noted. Lauryl methacrylate and (2-acetoacetoxy)ethyl methacrylate were purified by filtering through basic alumina columns to remove the inhibitor. AIBN was recrystallized in methanol.

Synthesis of linear polymer. Poly [(lauryl methacrylate)-co-(2-acetoacetoxy)ethyl methacrylate] (P(LMA-co-AAEMA)) was synthesized via RAFT polymerization. Briefly, monomers lauryl methacrylate (47.74 g, 0.19 mol) and (2-acetoacetoxy)ethyl methacrylate (4.47 g, 0.021 mol) with molar ratio 9:1 were dissolved in ethyl acetate (200 ml), and RAFT agent 2-cyano-2-propyl benzodithioate (0.111 g, 0.5 mmol) was added into the solution. The reaction mixture was stirred and purged with argon at 0 ℃ for 20 mins. Initiator AIBN (0.082 g, 0.5 mmol) was dissolved in ethyl acetate (15 ml) and added into the mixture. The reaction was carried out at 65 ℃ for 18 h in a capped 1000 ml round-bottom flask. The product was purified by precipitating in methanol and redissolving in toluene and precipitating from methanol 3 more times. The polymer was dried at room temperature overnight and then in a vacuum oven at 80 ℃ for 24 h to completely remove the solvents (38 g, 0.7 mmol, yield(%)=73).

RAFT polymer end group modification. To eliminate the reactivity of thiocarbonylthio group from the RAFT agent residing in the linear polymer,[1] end group modification was performed following the procedure previously reported.[2] The polymer (38 g, 0.7 mmol) was dissolved in toluene (200 ml), and the solution was stirred and purged with argon for 20 mins, and AIBN (2.35 g, 0.014 mol) was added into the solution with 20 molar equivalents relative to the polymer. The mixture was heated to 80 ℃ and reacted for 2.5 h. The product was precipitated in methanol to separate the polymer. A slightly pink polymer (29 g, 0.55 mol, yield(%)=76) was obtained after drying completely, confirming that most of the dithiobenzoate moiety was removed.

General procedure for metallopolymer preparation: The linear polymer (2 g, 0.04 mmol) was dissolved in anisole (10 ml) and metal acetate salts were dissolved in DMF (2 ml). The salt solution was added dropwise into the polymer solution under vigorous stirring. The liquid rapidly increased its viscosity due to the formation of cross-links. The solution was stirred continuously for 20 mins to ensure it was homogeneous. Solutions were then solvent-cast in a Teflon-lined petri dish and dried at room temperature for 24 h and then moved to the vacuum oven at 100 ℃ for 48 h to completely evaporate the solvents and acetic acid. For Ni-coordinated polymers, the samples were further heated at 110 ℃ for 24 h to remove H_2O as potential ligands in the coordination structure. To compare the influence of different Cu^{2+} concentrations, [acetoacetate ligand]:[Cu^{2+}] in the polymer was added in molar ratios of 20:1, 10:1 and 4:1, corresponding to cross-linking 5%, 10%, and 25% of the available ligands, respectively. To compare the influence of different metal species, [acetoacetate ligand]:[Zn^{2+}]/[Cu^{2+}]/[Ni^{2+}] in the polymer was added in a molar ratio of 4:1, corresponding to cross-linking 25% of the available ligands.

Crystal growth and X-ray crystallography. The single crystals were grown from a saturated solution of the Ni(II)-2-(acetoacetoxy)ethyl methacrylate (NiAAEMA) complex in chloroform by slow diffusion of hexane vapor at 4 ℃ over 2 weeks. X-ray diffraction data was collected on a Nonius Kappa CCD diffractometer with monochromated Mo Kα radiation (λ=0.71073 Å).[3] Accurate cell parameters were acquired by analyzing the amount of indicated reflections.[4] The diffraction image was processed by the software Mercury.[5] The structure was solved by direct methods (SHELXS-97) and refined against F^2 by full-matrix least squares methods (SHELXL-97).[6,7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically on calculated positions using a riding model. The isotropic displacement parameters U_{iso} were constrained to 1.5 times the U_{eq} value of their pivot atoms for terminal sp^3 carbon atoms, and 1.2 times for all other carbon atoms.

Gel permeation chromatography (GPC). The molecular weight and polydispersity of the linear polymer were measured by a Waters Ambient Temperature GPC. THF was used as the eluent with a flow rate of 1.00 mL/min. The polydispersity was determined based on polystyrene standards. GPC samples were prepared by dissolving the linear polymer in THF with a concentration of 1mg/ml and filter through a 0.45 um PTFE filter.

^{1}H nuclear magnetic resonance (^{1}H NMR). The ^{1}H NMR spectrum of the linear polymer was acquired on a Bruker Advance III HD 500 spectrometers. The polymer was dissolved in $CDCl_3$ and processed by 64 scans, with 30 s relaxation delay and 90° excitation pulse.

Differential scanning calorimetry (DSC). Polymer samples were loaded in Tzero aluminum pans and tested with a TA Instruments Q1000 MDSC. Samples were measured with a heating rate of 10 ℃/min and a cooling rate of 5 ℃/min in the range of -90 ℃ to 120 ℃ for one heating-cooling-heating cycle. Data from the second heating ramp was used. Glass transition temperatures (T_g) were determined from the inflection point of the curve.

Fourier-transform infrared (FTIR) spectroscopy. The IR spectra of the materials were collected by a Bruker Vertex V80V Vacuum FTIR system with the deuterated triglycine sulfate (DTGS) detector under the attenuated total reflection (ATR) mode. The spectral range of 4000 cm^{-1} to 600 cm^{-1} were collected. Samples were measured immediately after being taken out of vacuum oven at room temperature.

Rheology. The storage ($G'(\omega)$) and loss moduli ($G''(\omega)$) of the materials were measured by a TA Instruments DHR-3 rheometer with a 20 mm-diameter parallel plate. ~0.63 ml material was sandwiched by two plates with 2 mm thickness. Each sample was equilibrated at 25 ℃ for sufficient period of time to relax the normal force. A short frequency sweep starting from the highest frequency (629.324 rad/s) to lower frequencies with 1% strain amplitude was performed multiple times to make sure the data was converged. Then a full frequency sweep measurement was carried out.

Small-angle and wide-angle X-ray scattering (SAXS and WAXS). SAXS and WAXS were carried out at the Functional Materials Beamline (FMB) at the Cornell High Energy Synchrotron Source (CHESS). A diamond (220) side bounce monochromator was used to tune the x-ray energy to 15.89 keV,[8] and the beam size was set using slits. To collect WAXS data, a Pilatus 200K detector was positioned above and to the side of the transmitted beam, approximately 12 cm downstream of the sample. To collect SAXS data, a Pilatus 300K detector was positioned approximately 240 cm downstream of the sample. The SAXS flight path was helium filled. A beamstop photodiode was used to monitor transmitted intensity. The scattering pattern of silver behenate was used to calibrate the SAXS data, and the scattering pattern of lanthanum hexaboride was used to calibrate the WAXS data.

S2. Theoretical entanglement molecular weight

Theoretical entanglement molecular weights were calculated using BIOVIA Materials Studio Synthia,[8] which uses topological information to calculate quantitative structure-property relationships. The calculation was performed on a random copolymer at the specified ratio. The theoretical value of the entanglement molecular weight of the random copolymer P(LMA-co-AAEMA) consisting of 90% lauryl methacrylate and 10% (2-acetoacetoxy)ethyl methacrylate is ~70 kg/mol.

Parameters: temperature is at 298 K, the initial setup for approximate molecular weight is 50 kg/mol.

Table S1. Theoretical entanglement molecular weight at different ratios of two monomers.

Monomer 1	Mole fraction 1	Monomer 2	Mole fraction 2	Steric hindrance parameter	Characteristic ratio at 298K	Molar stiffness function	Entanglement molecular weight (g/mol)	Critical molecular weight (g/mol)	Entanglement length (Å)
LMA	1	AAEMA	0	2.480	12.296	49.028	74276	148553	734.2
LMA	**0.90**	**AAEMA**	**0.10**	**2.473**	**12.232**	**48.748**	**70687**	**141376**	**709.9**
LMA	0.50	AAEMA	0.50	2.445	11.960	47.632	57097	114193	612.4

S3. Gel permeation chromatography

The molecular weight and polydispersity of the linear P(LMA-co-AAEMA) with molecular ratio 9:1 were measured by GPC. The molecular weight and polydispersity remain the same before and after RAFT end group modification. The number average molecular weight (M_n) is 53 kg/mol and polydispersity (*PDI*) is 1.2.

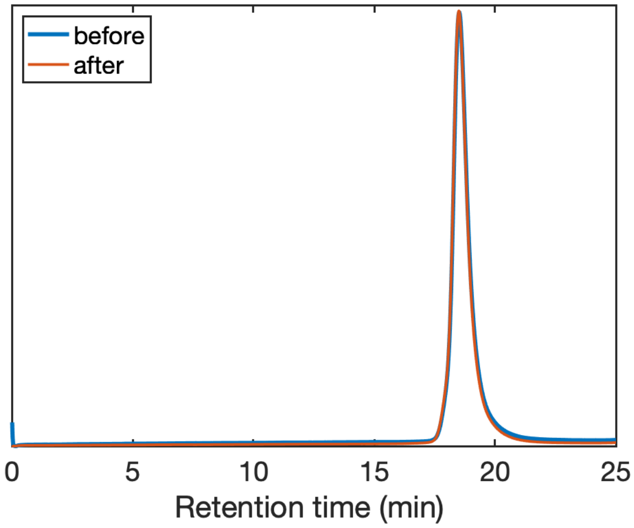

Figure S1. GPC plots of the linear polymer before (blue) and after (red) removal of the RAFT end group.

S4. ^{1}H Nuclear magnetic resonance

The ratio of the two monomers in P(LMA-co-AAEMA) was characterized by ^{1}H NMR. The integral area of the peaks located at 3.5-4.5 ppm have ratios a:b:c:d = 1:1:9:1, which corresponds to the different environments of the protons labelled in Figure S2. The peaks labelled as a, b, and d are from the monomer AAEMA, and the peak labelled as c is from the monomer LMA. The result indicates the ratio of the two monomers is 1:9. This verifies that the ratio of two monomers in the product is the same as the monomer ratio input in the reactants.

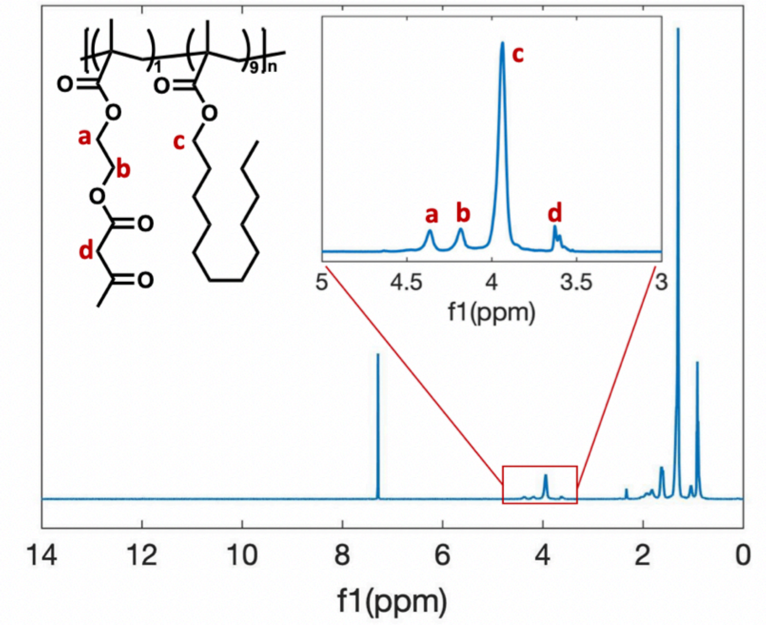

Figure S2. ^{1}H NMR of the linear polymer.

S5. Differential scanning calorimetry

The glass transitions of the linear polymer and of the metallopolymers were characterized by DSC, $T_g \approx -55°\mathrm{C}$ for all the samples.

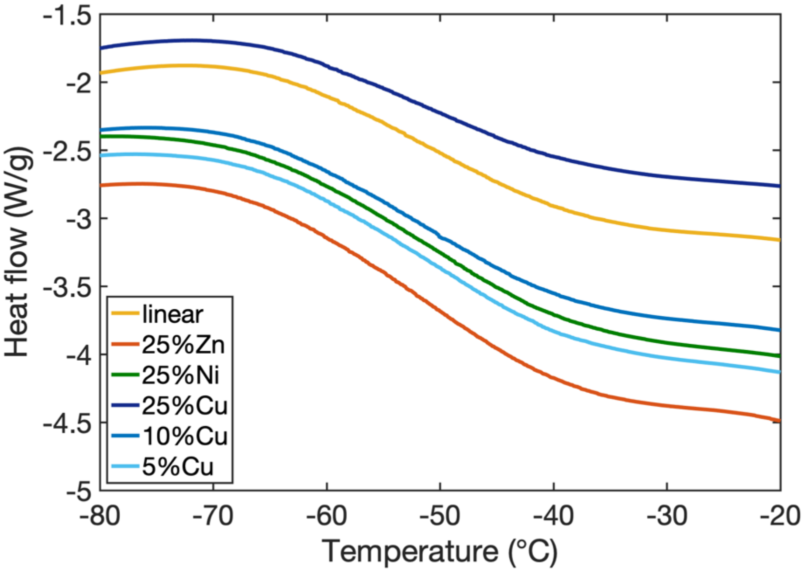

Figure S3. DSC of the linear polymer and the metal-coordinated polymers.

S6. Crystal structure

The crystal structure of NiAAEMA is shown in Figure S4. Six Ni(II) ions bond with the surrounding ligands from 2-(acetoacetoxy)ethyl methacrylate. Each Ni(II) center has an octahedral geometry. Most of the binding sites are occupied by the oxygen atoms from the acetoacetate group, while a few sites are occupied by the oxygen atom from water molecules. The Ni(II) centers interact with each other and form a bulky association site.

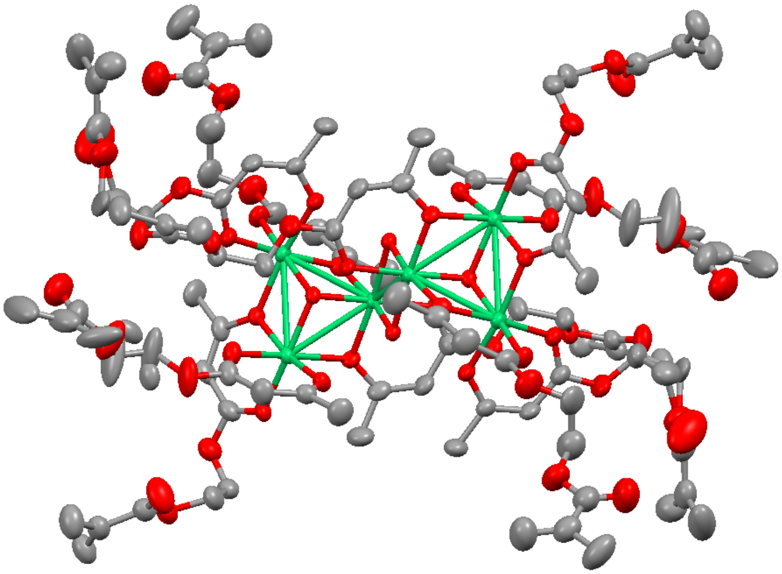

Figure S4. The crystal structure of NiAAEMA.

S7. Small-angle and wide-angle X-ray scattering

The SAXS data show no peak after the center of the beam, indicating no long-range order exists in any of the samples. For WAXS, the peak at $q = 13\,nm^{-1}$ (corresponding to the average distance of $2\pi/q = 0.48\,nm$) results from intermolecular scattering and the peaks at $q = 21.5\,nm^{-1}$ and $28\,nm^{-1}$ (corresponding to the average distance of $2\pi/q = 0.29\,nm$ and $0.22\,nm$, respectively) are from the periodicities along the polymer chains.[9]

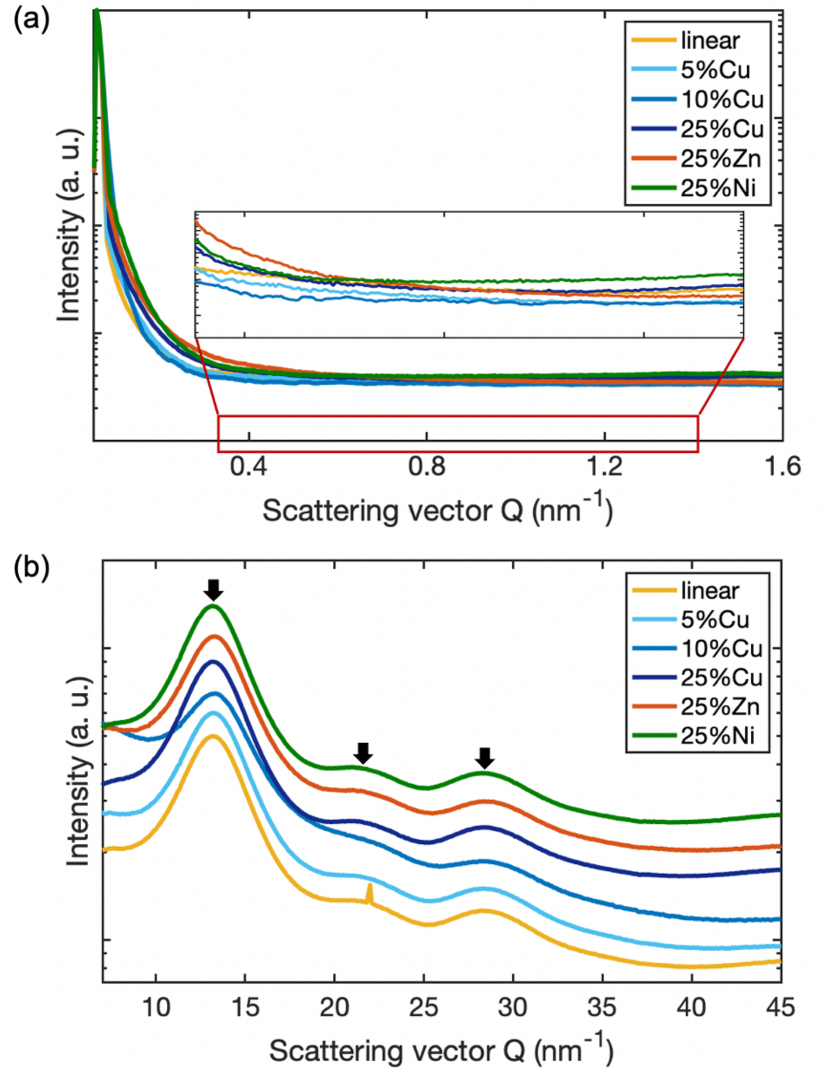

Figure S5. (a) SAXS and (b) WAXS of the linear polymer and the metal-coordinated polymers.

S8. Influence of ambient humidity

The sample of Ni(II) cross-linked polymers with 25% cross-linking ratios (**25%Ni dried**) was immediately characterized by IR spectroscopy and rheometer after being taken out from the vacuum oven. Then the same sample was exposed to an indoor environment for 2 weeks (**25%Ni in air**) and tested again. The coordination structure of the Ni(II) coordinated polymers was verified by FTIR (Figure S6a). Compared to the linear polymer, and the Ni(II) cross-linked polymer placed under vacuum, the Ni(II) cross-linked polymer placed at room environment coordinates with water from the ambient humidity. The increase of the peak height at ~1630 cm^{-1} verifies the presence of water molecules. The storage modulus of the Ni(II) cross-linked polymer after absorbing water is lower, which likely results from the changing of the Ni(II)-acetoacetate coordination structure. When more water molecules participate in the coordination, there are fewer Ni(II)-acetoacetate bonds, and thus the cross-linking is weaker.

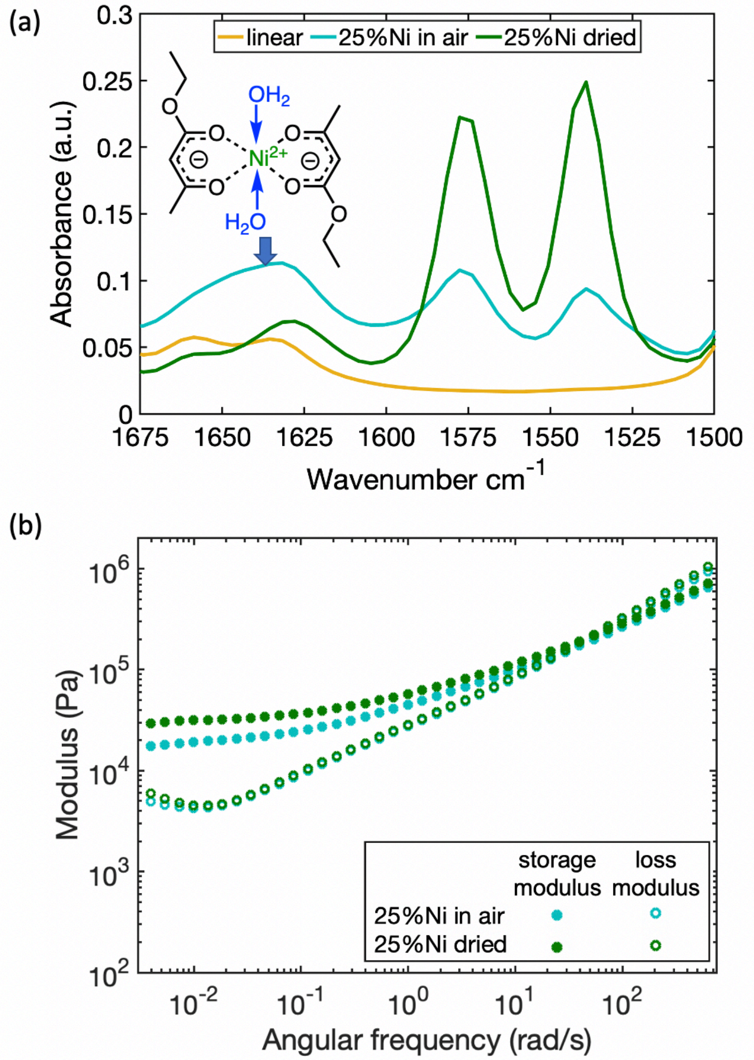

Figure S6. (a) FTIR spectra of the linear polymer and Ni(II) cross-linked polymers with 25% cross-linking ratios. (b) Rheology plot of **25%Ni**.

S9. Rheology data

The rheological measurements were performed multiple times for the linear polymer and metal-coordinated polymers. The mean values with standard error of the mean are given in Table S2.

Table S2. The storage and loss moduli of the linear polymer and the metal-coordinated polymers at the highest frequency measured.

Sample name	Angular frequency $\omega(rad/s)$	Storage modulus $G'(\times 10^5 Pa)$	Loss modulus $G"(\times 10^5 Pa)$	$\Delta G' = G'_{crosslinked} - G'_{linear}$ $(\times 10^5\ Pa)$	$\Delta G" = G"_{crosslinked} - G"_{linear}$ $(\times 10^5\ Pa)$	Avg # of cross-links per chain N_x
linear	629.324	3.4±0.1	5.7±0.1	0	0	0
5%Cu	629.324	4.0±0.1	6.6±0.1	0.6±0.2	0.9±0.2	1
10%Cu	629.324	4.8±0.1	7.6±0.1	1.4±0.2	1.9±0.2	2
25%Cu	629.324	8.5±0.2	12.7±0.2	5.1±0.3	7.0±0.3	5
25%Zn	629.324	4.9±0.2	7.6±0.4	1.5±0.3	1.9±0.5	5
25%Ni	629.324	6.8±0.2	9.8±0.3	3.4±0.3	4.1±0.4	5

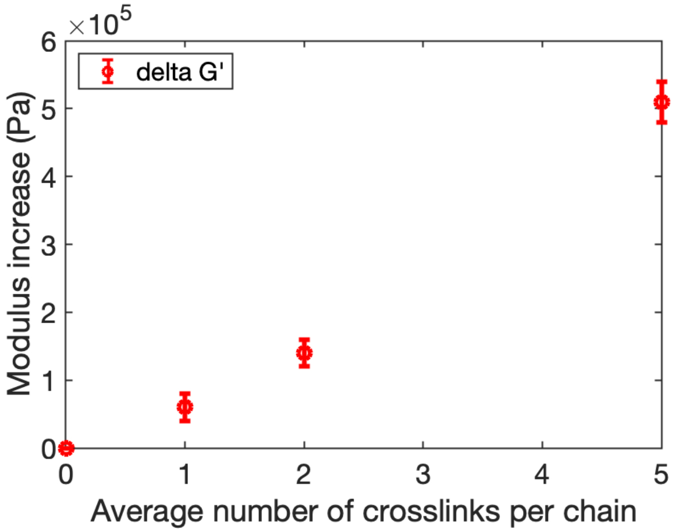

Figure S7. The increase of storage modulus with varying the average number of cross-links per chain for the Cu(II) coordinated polymer.

S10. Fitting methods and parameters

General parameters: Boltzmann constant $k = 1.38 \times 10^{-23}\, J/K$; temperature $T = 300\, K$; number of Kuhn monomers $N = 21$.

The fitting parameters of the linear and metal-coordinated polymers were obtained by a nonlinear iterative optimization algorithm using the MATLAB function *fminsearch* to minimize the following objective function:

$$L(\theta) = \sum_{\omega_i} \left[\log_{10}\left(G'_{fit}(\omega_i, \theta)\right) - \log_{10}\left(G'_{experiment}(\omega_i)\right)\right]^2$$

where ω_i is the angular frequency, θ is an array of fitting parameters (e.g., G_x and τ_x^*), $G'_{experiment}(\omega_i)$ is the storage modulus from the rheological data, and $G'_{fit}(\omega_i)$ is the storage modulus obtained from the model.

For the linear polymer, the fitting parameters in the Rouse model (Eq. 4) are the Rouse time $\tau_R = 0.4078$ s, the initial modulus $G_0 = 3.6 \times 10^5\, Pa$. The goodness of fit: $R^2 = 0.99$.

For the metal-coordinated polymers, the increase of the initial modulus G_x and the renormalized lifetime of the crosslink τ_x^* are fit by the method mentioned above.

The fitting parameters of **25%Ni** applied in the extended sticky Rouse-like modification for plotting Figure 7(b): the actual crosslink lifetime τ_x was assigned as a fitting parameter. To spread out the modes (p = 1 to 5), each was multiplied by a shift factor a_p with reference to τ_x. The initial modulus increase G_x was also a fitting parameter. The parameters for plotting 7(b) are

$[\tau_x, a_1, a_2, a_3, a_4, a_5, G_x] = [\, 0.19, 741.76, 584.88, 11.58, 2.02, 0.56, 4.52]$

S11. SI References

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