Multifunctional Polymers Built on Copper-Thioether Coordination

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Supporting Information

Materials Dichloromethane (DCM) (AR) was purchased from Nanjing black ants Biological Technology Co., Ltd. 2-(methylthio) ethanol (MTEA) (≥98%) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) (\geq 97%) were supplied by Shanghai Titan Technology Co., Ltd. Acrylic acid (≥99%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 4-dimethylaminopyridine (DMAP) (299%) was purchased from Shanghai Haibei Biotechnology Co., Ltd. Dimethylformamide (DMF) (99.5%) was provided by Sinopharm Group Chemical Reagent Co., Ltd. Butyl acrylate (BA) (99%, Sigma-Aldrich) and methyl methacrylate (MMA) (99.0%, Sigma-Aldrich) were purified through alumina oxide columns before using. Acetonitrile (MeCN) (AR) was supplied by Shanghai Ling Feng Chemical Reagent Co., Ltd. Cuprous Bromide (CuBr) and Cupric bromide (CuBr₂) were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.

Instrumentation

¹*H NMR* The Bruker Av400III HD instrument was used to measure samples at 400 MHz with Acetone-D or Chloroform-D as the solvent.

Gel Permeation Chromatography (GPC) The PL-GPC 220 (Polymer Laboratories) was operated to measure samples on at 40 $^{\circ}$ C in THF with polystyrene (PS) as the calibration standard. The detection was performed with a low rate of 1 mL/min.

Solid Mechanical Property Experiments The polymers were hot-pressing at 150 $^{\circ}$ C following ASTM standard D1708 to prepared the dog-bone-shaped samples (length: ~38 mm, width: ~15 mm, thickness: ~0.5 mm). Tensile tests were operated on a SANS E42.503 tensile tester with a displacement-speed control of 5.0 mm/min. An average over at least three measurements on three identical samples was used the reported results.

Small Angle X-ray Scattering (SAXS) SAXS experiments were carried out using the beamline (X-ray Diffraction and Scattering) at the National Synchrotron Radiation Laboratory (Hefei, China) with an X-ray wavelength of 0.154 nm. A Mar345 image plate (2300 × 2300 pixels with a pixel size of 150 mm) was employed to collect 2D SAXS patterns. Samples were prepared as 0.5 mm thin film and all measurements were taken with 10 minutes exposure time. SAXS data was analyzed by Fit2D software from European Synchrotron Radiation Facility, and are reported in units of arbitrary intensity. In all cases the scattering patterns were cylindrical symmetric and were therefore reduced to the 1-D form of intensity versus scattering wave vector magnitude, $q = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle.

Differential Scanning Calorimetry (DSC) The SDT-Q600 thermal analyzer (TA) was used to determined thermal transitions. The samples $(5\sim10 \text{ mg})$ were loaded into DSC pans, first heated to 130 °C at a rate of 40 °C/min and held to erase any thermal history that was quenched to -70 °C, then reheated to 130 °C at a rate of 20 °C/min. The glass transition temperatures were confirmed during the second heating run.

Ultraviolet-visible Light Detector (UV) Films were prepared through the hot-press approach. Then, these films were placed above hydrochloric acid with different time. After that, these films were irradiated under ultraviolet lamp, whose wattage was 500 W and wave length range was $350 \sim 450$ nm, at a certain time interval. And UV was conducted by a Shimadzu Autograph UV-2450 with the scan from 200 to 800 nm.

Cyclic Tensile Test The long-striped sample (length: \sim 38 mm, width: \sim 5 mm, thickness: \sim 0.5 mm) were prepared by Hot-press method. The Cycle Test was conducted through a SANS E42.503 tensile tester. The displacement-speed of the Cycle Test was controlled at 5.0 mm/min. Strains becoming greater than 25%, 50%, 100%, 150%, 200% and 250% were the termination condition of stretching process, the force becoming less than 0 N was the termination condition of recovery process.

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES): 100 mg sample was calcined at 600 °C for 1 h, the residual material was dissolved in a 25 mL volumetric flask with 4.8 mol/L of HCl and the concentration of Cu was measured by ICP-3000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The results were summarized in **Table S2**.

Experimental

Preparation of PMMA-b-P(BA-co-MTEA) [M₂₀₀-b-(B₃₇₈T₂₄₈)]. M₂₀₀-b-(B₃₇₈T₂₄₈) was prepared by adding PMMA (1.3 g, 0.065 mmol), BA (5.2 g, 5.8 mL, 40.6 mmol), MTEA (5.9736 g, 40.6 mmol), AIBN (2.1 mg, 0.013 mmol) in the 25 mL flask and 8 mL DMF as the solvent. The flask was degassed through three freeze-pump-thaw cycles and backfilled with nitrogen. Then the flask was placed in a water bath at 70 $\$ C and stirred for 9.5 h. After reaction, the polymer was precipitated three times in methanol and dried under vacuum for 2 h at 45 °C to obtain pink solids. Yield: 5.6g, 44.9%. GPC: M_n = 39k, M_w = 58k. ¹H NMR (Chloroform-D, δ , ppm) (**Figure S3**): 3.54 (-COO*CH*₃,3H), 3.98 (-COOCH₂CH₂CH₂CH₃, 2H), 1.53 $(-COOCH_2CH_2CH_2CH_3,$ 2H), 1.31 $(-COOCH_2CH_2CH_2CH_3,$ 2H), 0.87 (-COOCH₂CH₂CH₂CH₃, 3H), 4.14 (-COOCH2CH2SCH3, 2.642H), (-COOCH₂CH₂SCH₃, 2H), 2.08 (-COOCH₂CH₂SCH₃, 3H).

Preparation of PMMA-*co***-PBA-***co***-PMTEA** (**M**₂₁₃**-B**₃₂₆**-T**₃₁₇). M₂₁₃-B₃₂₆-T₃₁₇ was prepared by adding MMA (0.8 g, 0.8 mL, 7.99 mmol), BA (2.56 g, 2.9 mL, 20.0 mL),

MTEA (2.94 g, 20.0 mL), RAFT (7.08 mg, 0.03 mmol) reagent, AIBN(1.05 mg, 0.006 mmol) in the 25 mL reaction the flask and 2 mL DMF as the solvent. The flask was degassed through three freeze-pump-thaw cycles and backfilled with nitrogen. The flask was placed in an water bath at 70 $\,^{\circ}$ C and stirred for 4.5 h. The polymer was precipitated three times in methanol and dried under vacuum for 2 h at 45 °C to obtain pink solids. Yield: 3 g, 47.6%. GPC: $M_n = 42k$, $M_w = 63k$. ¹H NMR (Chloroform-D, δ , 3.96 (-COOCH₂CH₂CH₂CH₃, 3.52 (-COO*CH*₃,3H), 2H), 1.52 ppm): (-COOCH₂CH₂CH₂CH₃, 2H), 1.30 (-COOCH₂CH₂CH₂CH₃, 2H), 0.87 (-COOCH₂CH₂CH₂CH₃, 3H), 4.14 (-COO*CH*₂CH₂SCH₃, 2.64 2H), (-COOCH₂CH₂SCH₃, 2H), 2.08 (-COOCH₂CH₂SCH₃, 3H).

CuBr/CuBr₂ coordination with thioether polymer. M_{200} -*b*-($B_{378}T_{248}$)-CuBr (3%, 6.6%, 10.5%), M_{200} -*b*-($B_{378}T_{248}$)-CuBr₂ (7%), M_{213} - B_{326} - T_{317} -CuBr(7.4%) were prepared through a coordination of CuBr/CuBr₂ and thioether. These samples were prepared in the same procedure, but with the different mass ratios of CuBr/CuBr₂ and thioether polymer. For example, for M_{200} -*b*-($B_{378}T_{248}$)-CuBr (6.6%), 1.0 g polymer was dissolved in 6 mL of MeCN and added to 0.1 g CuBr with stirring until colloidal matter was separate out. The matter was then transferred to a Teflon mold and the solvent was allowed to evaporate for 24 h under ambient conditions. The sample was further dried at 45 °C in a vacuum oven.

Self-healing tests. The self-healing tests were performed at room temperature. The dog-bone-shaped samples were prepared by melt-compounding of polymers. The specimen was completely cut into halves and contacted for healing. The self-healing was performed under ambient conditions for 24 hours. The healed sample was used for tensile test.

Response towards HCl and H₂O₂. For HCl, M_{200} -*b*-($B_{378}T_{248}$)-CuBr (6.6%) was melt-compounded into thin films (2 cm × 2 cm × 0.1 mm) and covered on a beaker with 5 mL HCl (12 mol/L). UV-vis and photos were taken during the experiment. For

 H_2O_2 , M_{200} -*b*-($B_{378}T_{248}$)-CuBr (6.6%) was melt-compounded into a stick (3 cm x 0.3 cm x 0.05 cm) and then immersed into H_2O_2 solution (3% wt and 0.3% wt). Thin films (3 cm x 0.3 cm x 0.05 cm) were also utilized to test H_2O_2 solution (3% wt and 0.3% wt). Photos were taken during the experiment.

Estimation of Flory-Huggins Interaction Parameter χ

Based on the functional group contribution method,^{1,2} the solubility parameters of all components are estimated as:

 δ (MMA) = 9.18 $\sqrt{(cal/cm3)}$

 δ (BA) = 9.13 \checkmark (cal/cm3)

 δ (MTEA) = 9.68 $\sqrt{(cal/cm3)}$

For the second block P(BA-*co*-MTEA), it is a random polymer, according to the mixing rule, the equivalent solubility parameters are:

δ (B₃₇₈T₂₄₈) = 9.35 √ (cal/cm3)

Using the following relationship² for estimating χ :

$$\chi = \frac{\hat{V}_1}{RT} (\delta_1 - \delta_2)^2$$

where \hat{V}_1 is reference volume and we can use the MMA monomer volume, so $\hat{V}_1 = M/\rho = \frac{(100.12g/mol)}{(0.94g/cm^3)} = 106.51 \, cm^3/mol$ and R=1.987 cal/K

The result at 25 $^{\circ}$ C (298.15K) is:

 $\chi(M_{200}/B_{378}T_{248}) = 0.0052$, $\chi N = 4.30$, for this diblock, $T_{ODT} \approx 122$ °C



Figure S1. ¹H NMR spectrum for methyl thioethyl acrylate (META) monomers.



Figure S2. ¹H NMR spectrum for the PMMA block. The inset is the zoom-in spectrum displaying phenyl protons of the RAFT agent. The molecular weight of PMMA block was calculated by comparing the integrated peak areas for phenyl protons and methyl protons (3.6 ppm).



Figure S3. ¹H NMR spectrum for the diblock polymer, M_{200} -*b*-($B_{378}T_{248}$). The number of repeat units of BA and MTEA were determined by the integrated areas under peaks for BA and MTEA in the ¹H NMR spectrum.



Figure S4. ¹H NMR spectrum for the random copolymer, M_{213} - B_{326} - T_{317} .



Figure S5. SEC curves for the PMMA macroinitiator, M_{200} -b- $(B_{378}T_{248})$ block polymer and M_{213} - B_{326} - T_{317} random copolymer.

Table S1. Molecular characteristics of the synthesized polymers and the associated copper(I) bromide coordinated hybrid materials.

Samples	PMMA	M ₂₀₀ - <i>b</i> -(B ₃₇₈ T ₂₄₈)-CuBr ^c				M ₂₁₃ -B ₃₂₆ -T ₃₁₇ -CuBr ^c	
		0%	3%	6.6%	10.5%	0%	7.4%
M_n^{a}	11200	38600			42400		
$M_w^{\ a}$	12800	57500			62900		
PDI ^a	1.14	1.49			1.48		
$T_{g, BT} (C)^{b}$	-	-21.9	-6.0	9.9	27.5	-5.2	19.6
$T_{g,M}(\mathcal{C})^b$	98	93	_ d	- ^d	- ^d	-	-

^a M_{n} , M_{w} and Đ were determined by SEC at 40 °C using polystyrene standards and tetrahydrofuran (THF) as the mobile phase. ^bT_{g, BT} and T_{g, M} are the glass transition temperatures for B₃₇₈T₂₄₈ and PMMA phases, respectively. ^c M₂₀₀-*b*-(B₃₇₈T₂₄₈)-CuBr and M₂₁₃-B₃₂₆-T₃₁₇-CuBr are the block polymer and random copolymer in the work. The percentages 0%, 3%, 6.6% and 10.5% are the weight percent of CuBr added to polymers. ^d The glass transition temperature of PMMA was not observed in the hybrid materials.

Table S2. Copper content in polymers determined by Inductively CoupledPlasma Atomic Emission Spectroscopy (ICP-AES).

Samples		M ₂₁₃ -B ₃₂₆ -T ₃₁₇			
	CuBr (3%) ^a	CuBr (6.6%)	CuBr (10.5%)	CuBr ₂ (7%)	CuBr (7.4%)
$Cu (mg/L)^b$	52.3	118	185	79.0	130
$m_{Cu} (mg)^c$	1.3	2.9	4.6	2.0	3.2
$Cu(\%)^d$	1.3	2.9	4.6	2.0	3.2
$CuBr(\%)^e$	3.0	6.6	10.5	-	7.4
$CuBr_2(\%)^f$	-	-	-	7.0	-
$F_{Cu:T}^{g}$	0.16 : 1	0.33 : 1	1.1 : 1	0.21:1	0.27:1
$P_{Cu:T}^{g}$	0.09:1	0.21:1	0.34 : 1	0.14:1	0.19:1

^a CuBr (a%) or CuBr₂ (a%) was the polymer sample coordinated with a% (weight percentage) CuBr or CuBr₂. ^b Cu (mg/L): concentration of Cu in polymer (100 mg polymer was calcined at 600 $^{\circ}C$, the resulting residue was dissolved in a 25 mL volumetric flask with 4.8 mol/L of HCl and Cu (mg/L) measured by ICP-AES.

^c m_{Cu} : the actual weight of Cu in polymers ($m_{Cu} = \frac{Cu(\frac{mg}{L})}{10^3} * 25 mL$).

^d Cu (%): the weight percent of Cu in polymer (Cu (%)= $\frac{m_{Cu}}{m_p} * 100$, m_p : the weight of the coordinated polymers).

^e *CuBr* (%): the weight percent of CuBr in polymer (*CuBr* (%)= $\frac{Cu(\%)}{M_{Cu}} * M_{CuBr}$, M_{Cu} : The molar mass of Cu, M_{CuBr} : The molar mass of CuBr).

^f $CuBr_2$ (%): the weight percent of CuBr₂ in polymer ($CuBr_2$ (%) = $\frac{Cu(\%)}{M_{Cu}} * M_{CuBr_2}$, M_{CuBr_2} : The molar mass of CuBr₂).

^g $F_{Cu:T}$ and $P_{Cu:T}$ were the molar ratios of copper metal to thioether units in the feed and final product, respectively. $F_{Cu:T and} P_{Cu:T}$ were calculated by equation: $F_{Cu:T} \text{ or } P_{Cu:T} = \frac{m_{CuBr}/M_{CuBr}}{m_{polymer}/M_{W} \times N_{T}}$. M_{w} is the

molecular weight of the polymers; N_T is the repeat number of thioether units in a polymer chain. M_{CuBr2} should be applied in the equation when $CuBr_2$ is used.



Figure S6. Differential scanning calorimetry (DSC) curves of the M_{213} - B_{326} - T_{317} random copolymer and the CuBr coordinated material. Arrows indicate the glass transition temperatures.

Table S3. Tensile properties of pure polymers and their CuBr-coordinated materials

Samples	σ_b (MPa)	E (MPa) ^a	<i>Е</i> _b (%)	Toughness (MJ/m ³) ^b
M ₂₀₀ -b-(B ₃₇₈ T ₂₄₈)	0.3 ± 0.1	$0.1\ \pm 0.1$	$293~{\pm}43$	0.5
M_{200} - <i>b</i> -($B_{378}T_{248}$)-CuBr (3%)	$0.7\ \pm 0.1$	$0.3\ \pm 0.1$	$427\ \pm 58$	1.9

M ₂₀₀ - <i>b</i> -(B ₃₇₈ T ₂₄₈)-CuBr (6.6%)	2.0 ± 0.1	0.4 ± 0.1	665 ± 7	7.5
M ₂₀₀ - <i>b</i> -(B ₃₇₈ T ₂₄₈)-CuBr (10.5%)	7.0 ± 1.9	$4.4~{\pm}0.9$	$468~{\pm}51$	19
M_{213} - B_{326} - T_{317} - CuBr (7.4%)	$0.05\ \pm 0.1$	0.1 ± 0.1	$599~\pm70$	0.3
M ₂₀₀ -b-(B ₃₇₈ T ₂₄₈)-CuBr ₂ (7%)	$0.7\ \pm 0.4$	$2.0\ \pm 0.6$	34 ± 65	0.2
M ₄₁₀ - <i>b</i> -(B ₃₆₅ T ₂₅₇)-CuBr (6.1%)	5.2 ± 1.1	11 ± 3	$157\ \pm 31$	5.2

^a Room temperature Young's modulus (E) determined from the slope of the fitting line to the linear elastic regime of stress-strain curves. ^b Tensile toughness determined by integrating the area under stress-strain curves up to the specimen breaking point.

Calculation of recovery ratios in the cyclic tests:

Elastic Recovery =
$$\frac{\mathcal{E}_{\max} - \mathcal{E}_{0,\max}}{\mathcal{E}_{\max}}$$

Here, \mathcal{E}_{max} is the maximum strain being applied to the specimen; $\mathcal{E}_{0,max}$ is the strain in the relaxed state (stress is zero) after reaching the maximum strain.



Figure S7. Representative engineering stress *versus* strain curves for pure M_{200} -*b*-($B_{378}T_{248}$) block polymers. M_{200} -*b*-($B_{378}T_{248}$) (Healing) is the damaged specimen after 24 hours of self-healing. The damaged sample was very weak in mechanical strength.



Figure S8. Representative engineering stress *versus* strain curves for M_{213} - B_{326} - T_{317} -CuBr(7.4%). M_{213} - B_{326} - T_{317} -CuBr(7.4%)(Healing) was the damaged specimen after 24 hours self-healing.



Figure S9. XPS spectrum of Cl 2p for M₂₀₀-b-(B₃₇₈T₂₄₈)-CuBr(6.6%) after the treatment with HCl vapor. The peaks at 198 and 201 eV indicated the existence of chloride.



Figure S10. XPS spectrum of Br *3d* for (A) M_{200} -*b*-($B_{378}T_{248}$)-CuBr(6.6%) (Black curve) polymers without any treatment; (B) Polymers treated by H_2O_2 (3% wt) solution (Red curve); (C) Polymers after the treatment with HCl vapor (Blue). No obvious shift of peaks for Br *3d* was observed during the experiment, indicating that the state of bromine was not influenced during these treatments.



Figure S11. Photographs of M_{213} - B_{326} - T_{317} -CuBr(7.4%) thin films (2 cm × 2 cm × 0.1 mm) after exposure to HCl vapor for different time intervals.



Figure S12. Photographs of M_{200} -*b*-($B_{378}T_{248}$)-CuBr(6.6%) thin films (2 cm × 2 cm × 0.1 mm) after emerged into H_2O_2 (3% wt) solution for different time intervals.



Figure S13. Photographs of M_{213} - B_{326} - T_{317} -CuBr(7.4%) thin films (2 cm × 2 cm × 0.1 mm) after emerged into H_2O_2 (3% wt) solution for different time intervals.



Figure S14. Photographs of M_{200} -*b*-($B_{378}T_{248}$)-CuBr(6.6%) sticks (3 cm × 0.3 cm × 0.05 cm) after immersed in H_2O_2 solution (0.3% by weight) for different time intervals.



Figure S15. ¹H NMR spectrum for M_{200} -*b*-($B_{378}T_{248}$)-CuBr(6.6%) after treating with H_2O_2 . Part of the thioether groups are oxidized into sulfoxides as shown in the ¹H NMR spectrum. The partially oxidized polymers became slightly soluble in water.



Figure S16. IR spectra for M_{200} -*b*-($B_{378}T_{248}$)-CuBr(6.6%) before (black) and after (red) treating with H_2O_2 .



Figure S17. XPS spectrum of Cu 2p for (A) M₂₀₀-*b*-(B₃₇₈T₂₄₈)-CuBr(6.6%) (Black curve) polymers without any treatment; (B) Polymers treated by H₂O₂ (3% wt) solution (Red curve). Peaks at 934 eV and satellite peaks at 943, 963 eV matched with typical XPS spectrum of CuO.



Figure S18. The mixture of CuBr and H_2O_2 solution (3% by weight). Brown color was immediately observed when adding H_2O_2 .

References

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- 2. Hiemenz, Paul C., and Timothy P. Lodge. *Poly. Chem.* CRC press, 2007; pp 276-277.