Thermal-healable and shape memory metallosupramolecular poly(n-butyl acrylate-co-methyl methacrylate) materials

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Supporting Information

Experimental section

Materials: Acryloyl chloride, N-methyl-1,2-benzenediamine dihydrochloride which were purchased from Best reagent company. Zinc trifluoromethanesulfonate (Zn(OTf)₂), europium trifluoromethanesulfonate (Eu(OTf)₃) were purchased from Aladdin reagent corporation. Ethylene glycol dimethyl acrylate (EGDMA) was used as received without any treatment. Monomers including methyl methacrylate (MMA), butyl acrylate (BA) were obtained by reduced pressure distillation. Azodiisobutyronitrile (AIBN) was recrystallized from methanol prior to use. Solvents were used as supplied, with the exception of dimethyformamide (DMF), acetone, triethylamine, dichloromethane (DCM) and THF. Acetone and DCM were dried over CaCl₂ and distilled. THF were distilled from metal Na and benzophenone prior to use. Anhydrous DMF was obtained by reduced pressure distillation after dried over CaH₂. The chain transfer agent (CTA) S,S'-bis(R,R'-dimethylacetic acid) trithiocarbonate was synthesized according to reference.¹

Synthesis of 4-hydroxy-2,6-bis-(1'-methyl-benzimidazolyl)pyridine (compound 1, HO-Mebip)

Chelidonic acid and chelidamic acid were synthesized as literature reported.² Sodium methylate (8.41g, 155.7 mmol) and N-methyl-1,2-benzenediamine dihydrochloride (15.41g, 79 mmol) were dissolved in 250 ml methanol, then the solution was stirred overnight. The brownish red N-methyl-1,2-benzenediamine (NMB) was obtained by filtration and evaporation of solvent in vacuum. Chelidamic acid (7.41 g, 40.5 mmol) and 25 ml H₃PO₄ were then mixed with the remained NMB, the reaction was left to react for 10 h at 205°C.

After reaction, the dark blue mixture was poured into 700ml cold water and was stirred to form blue precipitate. After filtration, the precipitate was collected and the filtrate was neutralized by NaOH (5M) until blue precipitate once again occurred. Then the blue precipitates were suspended in 800 ml hot K_2CO_3 solution (10% wt). The mixture was stirred at 90 °C until the color of all the solids turned into pink. Next, the mixture was cooled down and was filtered. The obtained pink solids were re-dissolved in a 600 ml hot methanol to form red solution. The solution was cooled and was further neutralized by adding 1.0 M HCl solution dropwise until it turned to dark blue. The product was collected as light gray solids and dried in vacuo.

Yield: 9.6 g, 67%

¹H NMR (400 MHz, DMSO-d₆, δ): 4.24 (s, 6H, -NCH₃), 7.67 (d, *J* = 8.0 Hz, 2H, phenyl-H),
7.75 (d, *J* = 7.6 Hz, 2H, phenyl-H), 7.79 (s, 2H, phenyl-H), 11.37 (s, OH).
¹³C NMR (100 MHz, DMSO-d₆, δ): 32.48 (CH₃), 110.70 (Ar), 112.50, 119.40, 122.33,
123.08, 137.02, 141.98, 149.84, 150.90, 165.16.



Figure S1. 400 MHz ¹H NMR spectrum of 1 in DMSO- d_6



Figure S5. 100 MHz 13 C NMR spectrum of 1 in DMSO-d₆



Figure S2. 400 MHz ¹H NMR spectrum of chelidonic acid in DMSO-d₆



Figure S3. 400 MHz ¹H NMR spectrum of chelidamic acid in DMSO-d₆

Synthesis of 2-(2,6-Bis(1-methyl-1H-benzo[d]imidazol-2-yl)pyridin-4-yloxy)-

nonan-1-ol (compound 2, BIP-OH)

The self-made HO-Mebip or compound 1 (7.5 g, 21.1 mmol) and K_2CO_3 (12 g, 87.0 mmol) were charged into dry THF with stirring to form uniform mixture. Until the color of mixture turned into red, 2-bromoethanol (13.2 g, 105.7 mmol) was added while stirring and refluxed at 85 °C for 24h. After removing heat, the solvent was excluded by rotary evaporator. The remained solids were resuspended in boiling toluene and filtered directly from the boiling suspension. The product was recrystallized from toluene.

Yield: 6.8 g, 81%

¹H NMR (400 MHz, DMSO-d₆, δ): 3.83 (d, *J* = 2.4 Hz, 2H, -OCH₂CH₂OH), 4.26 (s, 6H, -NCH₃), 4.32 (d, *J* = 4.0 Hz, 2H, -OCH2-), 7.33 (m, 2H, phenyl-H), 7.37 (m, 2H, phenyl-H), 7.70 (d, *J* = 8.0 Hz, 2H, phenyl-H), 7.78 (d, *J* = 7.6 Hz, 2H, phenyl-H), 7.92 (s, 2H, phenyl-H). ¹³C NMR (100 MHz, DMSO-d₆, δ): 32.51 (CH₃), 59.27, 62.83, 70.31, 110.79 (Ar), 111.17, 119.44, 122.42, 123.21, 141.92, 149.57, 150.90, 165.81.



Figure S4. 400 MHz ¹H NMR spectrum of 2 in DMSO-d₆



Figure S5. 100 MHz 13 C NMR spectrum of 2 in DMSO-d₆

Synthesis of 2-(2,6-Bis(1-methyl-1H-benzo[d]imidazol-2-yl)pyridin-4-yloxy)nonyl acrylate (compound 3, Mebip-Ac)

Compound 2 (6 g, 15.0 mmol), triethylamine (3.4 ml, 24.4 mmol), dichloromethane (600 ml) were charged to a 1 L round bottom flask, then the solution was kept stirring at 0 $^{\circ}$ C for 2h. The acryloyl chloride (2 ml, 24.5 mmol) dissolved in dichloromethane (20 ml) was added into the above solution dropwise and the mixture was left to react for 4h at 0 $^{\circ}$ C, then 24h at room temperature. After reaction, the solution was washed and extracted with NaHCO₃ (1% wt) to remove remained reagents. The organic layer was collected, dried over sodium sulfate, filtered, and concentrated in vacuum. The product was collected and was further purified via column chromatography (CH₂Cl₂/MeOH).

Yield: 3.6 g, 51%

¹H NMR (400 MHz, CDCl₃, δ): 4.24 (s, 6H, -NCH₃), 4.51 (d, J = 4.4 Hz, 2H, -OCH₂CH₂OH), 4.59 (d, J = 4.4 Hz, 2H, -OCH2-), 5.88 (d, J = 10.4 Hz, 2H), 6.23 – 6.11 (m, 2H),6.45 (t, J = 14.8 Hz, 2H), 34 (m, 6H) , 7.87 (d, J = 7.4 Hz, 2H), 7.99 (s, 2H, phenyl-H) ppm. ¹³C NMR (100 MHz, CDCl₃, δ): 32.57, 62.25, 66.39, 76.85, 109.98, 111.71, 120.14, 122.88, 123.64, 127.90, 131.63, 137.19, 142.45, 150.11, 151.26, 165.90 ppm.



Figure S6. 400 MHz ¹H NMR spectrum of 3 in CDCl₃



Figure S7. 100 MHz ¹³C NMR spectrum of 3 in CDCl₃

Synthesis of copolymer (CP)

Butyl acrylate, methyl methacrylate, monomer compound **3**, CTA, AIBN were charged into dry DMF (Table S1), then the mixture was reacted at 70 $^{\circ}$ C for 24h under nitrogen. After polymerization, the solution was poured into cold MeOH/H₂O (v/v 9:1) to obtain polymer precipitate, and then was dried in vacuum at 50 $^{\circ}$ C.



Figure S8. 400 MHz ¹H NMR spectra of copolymers with 3%, 5%, 7% Mebip respectively in CDCl₃ and the impurities observed at δ ~2.9 is little amount of DMF.

Table S1. The feeding ratio of monomers and the composition of the final copolymer determined from ¹H NMR

Sample	f _{BA}	f _{MMA}	f _{Mebip-Ac}	F _{BA}	F _{MMA}	F _{Mebip-Ac}
CP-3	64.7	32.3	3	64.4	32.4	3.2
CP-5	63.3	31.7	5	61.9	32.7	5.4
CP-7	61.9	31.1	7	62.6	29.8	7.6

 f_x repesents the feeding ratio of each monomer, F_x corresponds to the final ratio of each monomer in the copolymer (x=BA, MMA, Mebip-Ac).



Figure S9. 100 MHz ¹³C NMR spectra of copolymers with 3%, 5%, 7% Mebip respectively in CDCl₃.

Table S2. Composition of the carbonyl carbon resonances of BA(B) and MMA(M) centered sequences calculated from peak area of ¹³C NMR spectra.

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Sample	1	2	3	4	5	6	7
CP-3	0.02	0.12	0.09	0.15	0.26	0.10	0.26
CP-5	0.03	0.15	0.10	0.14	0.24	0.11	0.23
CP-7	0.03	0.10	0.09	0.13	0.26	0.12	0.27

According to the literature^{3,4}, Peak 1 was assigned to MMM triads; peak 2 to MMM, BMM and MMB; peak 4 to MMM, BMM, MMB and BMB; and peak 6 to the BMB triad. Peak 3, 5, and 7 corresponds to the sequences of B-centered MBM, MBB and BBB triad respectively.

Synthesis of MSP series and the control samples:

Synthesis of the MSP sample : typically, In a 50 mL beaker the desired amount of the selfmade copolymer (CP series) was dissolved in chloroform (100 mg/ml). The Zn(OTf)₂ in acetonitrile (100 mg/mL) was added into the copolymer solution. The mixture turned into gel in 1 min after adding metal salts. Then the gel was dried at 70 $^{\circ}$ C for 4h and at 80 $^{\circ}$ C for 12h to remove the solvent in vacuum. The as-prepared solids were compression moulded at 170 $^{\circ}$ C to obtain a semi-transparent vellow rectangle sheet with a thickness of ~1000 µm.

Synthesis of the Control-1 (Eu-based MSP) sample: The method of Control-1 follows the same procedure with MSP-5 by using $Eu(OTf)_2$, while the compression moulding temperature dropped to 130 °C due to the weaker binding of Eu-Mebip.

Synthesis of Control-2 sample: MMA and BA with a certain mole ratio were mixed with CTA, AIBN, EGDMA (The recipe is shown in Table S1). Subsequently, the mixture was transferred into a glass mold (2 mm in height) sealed with silicone rubber and polymerized at 70 $^{\circ}$ C for 24 hours. The yellow transparent polymer was then taken out from the glass mold and dried in vacuum at 80 $^{\circ}$ C for 5 h to remove remained unpolymerized monomers.

Table S3. Polymerization recipes for P(MMA-BA) copolymer with Mebip ligands							
Sample	MMA	BA	Mebip-Ac/EGDMA	CTA	AIBN	DMF	Reaction
	(mmol)	(mmol)	(mmol)	(mmol)	(mmol)	(ml)	time (h)
CP-3	34.5	69.0	3.2	0.53	0.31	46	24
CP-5	20.3	40.5	3.2	0.32	0.19	28	24
CP-7	14.2	28.3	3.2	0.23	0.14	20	24
Control-2	20.3	40.5	3.2	0.32	0.19		24
Control-3	20.3	40.5		0.32	0.19		24

The co-monomers of CP copolymers are Mebip-Ac, BA, MMA. Control-2 is the chemically crosslinked poly(BA-MMA-EGDMA). Control-3 is the linear copolymer poly(BA-MMA) which is a flowing liquid at 25°C.

CP-3: ¹H NMR (400 MHz, CDCl₃, δ): 0.92-2.24 (260H), 3.58 (30H), 4.02 (40H), 4.25 (6H),

4.48 (4H), 7.38-7.48 (6H), 7.88-8.01 (4H)

CP-5: ¹H NMR (400 MHz, CDCl₃, δ): 0.92-2.24 (156H), 3.58 (18H), 4.02 (24H), 4.25 (6H),

4.48 (4H), 7.38-7.48 (6H), 7.88-8.01 (4H)

CP-7: ¹H NMR (400 MHz, CDCl₃, δ): 0.92-2.24 (104H), 3.58 (12H), 4.02 (16H), 4.25 (6H),

4.48 (4H), 7.32-7.48 (6H), 7.88-8.01 (4H)



Fig S9. GPC traces of the copolymer with Mebip ligand

Table S4. GPC results of the	copolymers	synthesized v	via RAFT
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Polymer	Mn	Mw	PDI	Content of Mebip
	(g/mol)	(g/mol)		by ¹ H NMR
CP-3	13515	26384	1.79	3.2%
CP-5	9815	20409	2.07	5.3%
CP-7	9781	21008	2.14	7.6%

Sample	$\operatorname{Tg}(^{\circ}\mathbb{C})$	$Tg_1(^{\circ}C)$	T_{g2} (°C)	$T_{f}(^{\circ}C)$
	by DSC	by DMA	by DMA	by DMA
MSP-3	-0.5	24.0	68.4	95
MSP-5	6.4	39.0	79.1	140
MSP-7	15.2	46.8	83.0	160

Table S5. A summary of the thermal behavior of MSPs



Figure S10. Mechanical an self-healing properties of Eu-based MSP (Contro-1)



Figure S11. Tan δ of Eu-based MSP (Contro-1)

Figure S11 shows that there is just one phase transition, i.e. glass transition. The orderdisorder transition appeared in the Zn-based MSP material is not observed in the Eu-based MSP sample.



Figure S12. Fluorescence spectra of MSP-5 sample (a) at various heating temperatures from 25 $^{\circ}$ C. (b) at various cooling time from 160 $^{\circ}$ C.

To verify the molecular mechanism of healing process, the fluorescence spectropy was utilized to detect the variation of metal-ligand interaction with the temperature. As temperature rises, the fluorescence emission intensity drops and the characteristic emission wavelength maximum shifts to a larger value possibly due to the disassociation of metalligand bond (**Figure S12 (a)**). After cooling, the the fluorescence emission intensity recovers to a certain degree and the characteristic emission wavelength maximum shifts back to original one. These results indicate that the Zn-Mebip metal-ligand bond can break at higher temperature and reform at lower temperature (**Figure S12 (b)**).

References

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