Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

for

Scorpion-Inspired Fluorescent Polymers

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1. EXPERIMENTAL SECTION

Materials: Vinylboronic acid pinacol ester, 4-bromophthalic anhydride and 1,6-dibromohexane were obtained from Shanghai Taitan Scientific Co., Ltd. Tetrakis (triphenylphosphine) palladium (0) was purchased from Energy Chemical Reagent Company. 1,6-Hexanediol was purchased from Ourchem Reagent Company. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was supplied by Shanghai McLin Biochemical Technology Co., Ltd. Methyl acrylate (MA, AR, stabilized with hydroquinone monomethyl ether), acrylic acid (AA, CP), triethylamine (TEA, AR), potassium carbonate, dichloromethane (DCM, AR), N,N-Dimethylformamide (DMF, AR) and 1,4-dioxane (AR) were purchased from China National Medicines Corporation Ltd. LB solid medium powder was purchased from AngelYeast Co., Ltd. Four Gram-positive bacteria (*S. aureus ATCC6538*, *S. aureus AB94004*, *S. epidermidis AB208187*, *S. epidermidis AB208188*), two Gram-negative bacteria (*E. coil ATCC8739*, *E. coil ATCC25922*), Ampicillin (Amp) and Vancomycin (Van) were purchased from Beyotime Biotechnology. The reactants were used without further purification except for AA, which was purified via vacuum distillation, while MA was filtrated through a basic alumina column to remove the inhibitor and AIBN was recrystallized in ethanol.

Preparation of PMDA-x.

The film of PMDA-x was prepared by free radical polymerization. (where x denotes the molar ratio of MA to AA.) As shown in **Scheme 1c**, MA (413.2 mg, 4.8 mmol), AA (144.1 mg, 2.0 mmol), DVMDE (1 mol%, 37.3 mg) and 2,2'-Azobis(2-methylpropionitrile)

(AIBN, 11.2 mg, 0.068 mmol) were dissolved in 1,2-dioxane (3 mL). The mixture solution was then added in a 10-mL round-bottom flask under N_2 atmosphere. The reaction was performed at 70 °C in an oil bath for 2 h. Then, the prepolymer was transferred to a polytetrafluoroethylene (PTFE) mold, and dried in an oven at 80 °C for 16 h to give the transparent film of PMAD-x.

Preparation of Fluorescent Anti-Counterfeiting Pattern.

The polymethyl methacrylate (PMMA) film and quartz glass with good optical transparency and non-fluorescence were chosen as the substrate material. The template of the pattern of East China Normal University was attached on the surface of the PMMA film or quartz glass, and then a solution of pre-PMAD was dropped evenly on the pattern template surface. Finally, the template was removed and the PMAD-coated PMMA film or quartz glass was dried in air to form a colorless and transparent pattern.

Antimicrobial activity screening of PMAD film.

The suspension of each microorganism was adjusted to 0.5 McFarland standard (about 150 × 106 CFU (Colony Forming Units)/mL) in sterile NaCl solution (0.9%). With the similar method to the Kirby-Bauer procedure (A), the determination of antimicrobial activity of the polymers of PMAD was performed in vitro in Petri plates. The films of PMAD were cut into disc-shaped pieces with the diameter of 10 ± 0.5 mm in aseptic condition. Luria-Bertan Broth agar medium buffered at pH 7.2 ± 0.2 (for bacteria) were used. Before testing, the respective media in Petri dishes were inoculated using swabs carrying the tested bacteria. The disc-shaped pieces of PMAD

were placed directly onto the agar surface and incubated at 37 °C overnight. The antimicrobial properties of PMAD were expressed by the inhibitory effects on microbial growth based on the growth inhibition zone (giz) diameter (in mm) around the pieces of PMAD. All experiments were performed in triplicate.

Quantification of the antimicrobial activity of PMAD film.

To determine the sustained inhibitory effect of the PMAD-x film against gram-positive bacterium, we designed a continuous bacteriostatic test. We cut each film of PMAD to a 10-milligram disc and put it into a 1.5 mL tube with bacterial. Then incubation was proceeded overnight at a constant temperature of 37 °C, and the average antimicrobial performance was calculated using formula: *Antibacterial rate* =1-A/A_0, where A_0 is the absorbance at 630 nm of bacterial without film, and A is the absorbance at 630 nm of experimental group.

Measurements. ^{1}H NMR spectra were carried out on a Varian Mercury Plus 500 MHz instrument with $CDCl_3$ and DMSO-d_6 as solvents at room temperature. Fourier transform infrared (FT-IR) spectra were recorded on a NEXUS 670 FTIR spectrometer from 3200 to 600 cm^{-1}. High-resolution mass spectrometry (HRMS) was performed on an Agilent 1290 Infinity UHPLC system coupled with a Bruker maXis impact mass spectrometer. The stress–strain curves were recorded at room temperature on a HY-0580 Tension Instrument (Shanghai hengyi precise instrument limited company). The elastomers were cut to rectangle strips (size: 20.0 mm × 3.0 mm ×1.0 mm) and fixed by two sample holders. A 50 N load cell was used, and the tensile speed was constant at 50 mm min^{-1}. Thermogravimetric analysis (TGA) was performed in a nitrogen

atmosphere at a heating rate of 10°min^{-1} (TGA/SDTA851e, Mettler Toledo, Switzerland). Differential Scanning Calorimetry (DSC) was performed in a nitrogen atmosphere at a heating rate of 10° min^{-1} (TA Instruments Q2000, Waters, America). The UV–vis absorption measurements (UV-1800, Shimadzu, Japan) of the PMAD films were performed over a wavelength range from 200 to 800 nm. The transparency of PMAD films were determined by a UV–vis spectrophotometer (UV-1800, Shimadzu, Japan) with quick mode from 200 to 800 nm. PL emission spectra were recorded on a fluorometer (Varioskan, Life Technologies, Singapore) at an excitation wavelength of 285 nm. The thickness and size of all the films of PMAD were constant for the fluorescence tests. The sample was placed on a mica sheet and an optical microscope image of the damage state was recorded on a polarizing microscope (Axio Scope. A1, Prussia Instruments Co., Ltd), obtained data on self-healing of the surface film.

2. Synthetic Procedures[1]

2.1 Synthesis of the compound divinyl macrocyclic diphthalate ester (DVMDE)

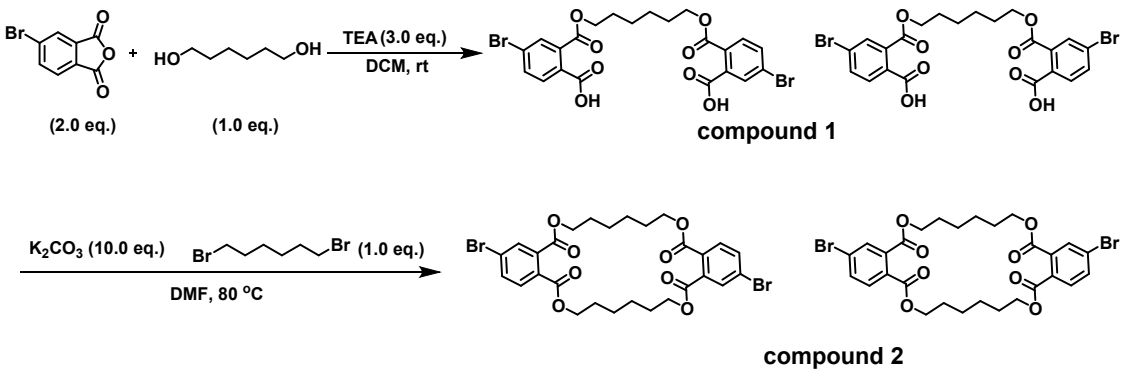
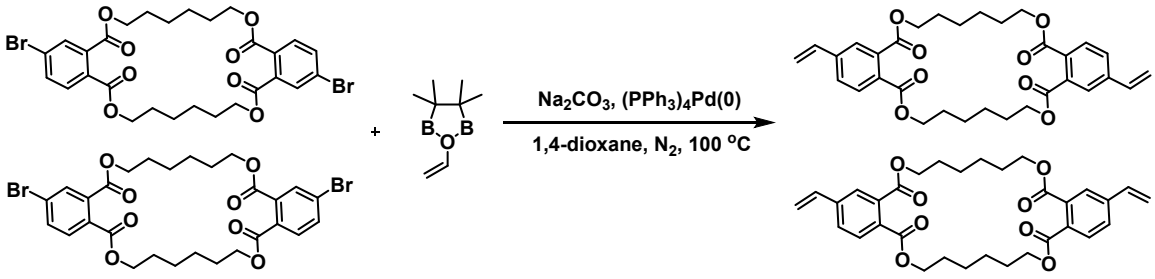


Figure S1. Synthesis of the compound 1 and 2.

Triethylamine (16.8 mL, 120 mmol) was added to a solution of 4-bromophthalic

anhydride (18.16 g, 80 mmol) and 1,6-Hexanediol (4.72 g, 40 mmol) in CH_2Cl_2 (75 mL). The solution was stirred at room temperature (rt) for 4 h. After completion of the reaction, under reduced pressure removal solvent to give the crude product of compound **1** as a yellow oil. ^{1}H NMR (500 MHz, DMSO) (Figure **S3**) δ 7.93 – 7.78 (m, 4H), 7.67 (m, 2H), 4.22 (t, J = 6.6 Hz, 4H), 1.67 (d, J = 6.0 Hz, 4H), 1.39 (s, 4H). HRMS (ESI) ([M + Na]$^+$, $C_{22}H_{20}Br_2O_8Na$): calcd, 595.1937; found, 595.1921.

Compound **1** (11.44 g, 20 mmol) and K_2CO_3 (27.65 g, 200 mmol) were dissolved in 150 mL of dimethylformamide (DMF), and the solution was stirred at rt for 1 h. Then, 1,6-dibromohexane (4.8 g, 20 mmol) was added to the solution and stirred at 80 °C for 24 h. Reaction detection by TLC until reaction completion. After cooling on ice, the mixture was extracted with ethyl acetate (100 mL × 3). The organic layer was washed with H_2O (100 mL × 3). The solvent was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 2/1) to give pure compound **2** as a white solid (16.6% yield). ^{1}H NMR (500 MHz, $CDCl_3$) (Figure **S4**) δ 7.84 (s, 2H), 7.68 (m, 2H), 7.63 (d, J = 8.3 Hz, 2H), 4.31 (m, 8H), 1.76 (m, 8H), 1.52 – 1.41 (m, 8H). HRMS (ESI) ([M + Na]$^+$, $C_{28}H_{20}Br_2O_8Na$): calcd, 677.3411; found, 677.3415.



compound 2 **DVMDE**

Figure S2. Synthesis of the compound DVMDE.

A double-necked round-bottom flask equipped with a reflux condensing apparatus was charged with compound **2** (2.6 g, 4 mmol) dissolved in 30 ml 1,4-dioxane, anhydrous Na_2CO_3 (4.14 g, 40 mmol) in 10 ml H_2O and vinylboronic acid pinacol ester (2.4 g, 10 mmol) under nitrogen atmosphere and stirred well at room temperature. Then add tetrakis (triphenylphosphine) palladium (0) (369.8 mg, 0.32 mmol). After stirring at 100 °C for about 12 h (by TLC assay), the solution was cooled to room temperature. The crude product was extracted with water and ethyl acetate, and the aqueous phase was extracted three times with ethyl acetate. The combined organic phases were dried by anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to give the pure product **DVMDE** as a white solid (yield: 78%). ^{1}H NMR (500 MHz, $CDCl_3$) (Figure **S5**) δ 7.79 – 7.61 (m, 4H), 7.52 (d, J = 8.0 Hz, 2H), 6.72 (m, 2H), 5.87 (d, J = 17.6 Hz, 2H), 5.36 (m, 2H), 4.29 (q, J = 6.4 Hz, 8H), 1.75 (s, 8H), 1.45 (s, 8H). HRMS (ESI) ($[M + Na]^+$, $C_{32}H_{36}O_8Na$): calcd, 571.2330; found, 571.2332.

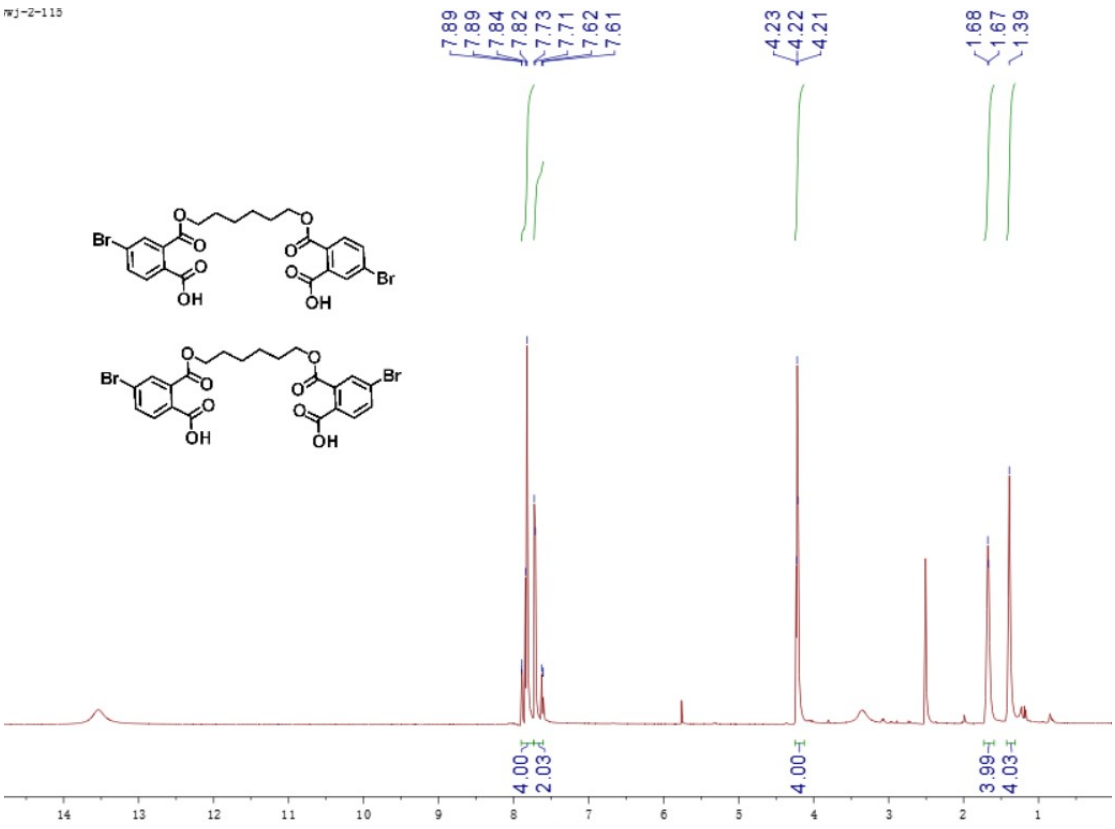


Figure S3. ^{1}H NMR spectrum of compound **1** (DMSO-*d6*, 500 MHz).

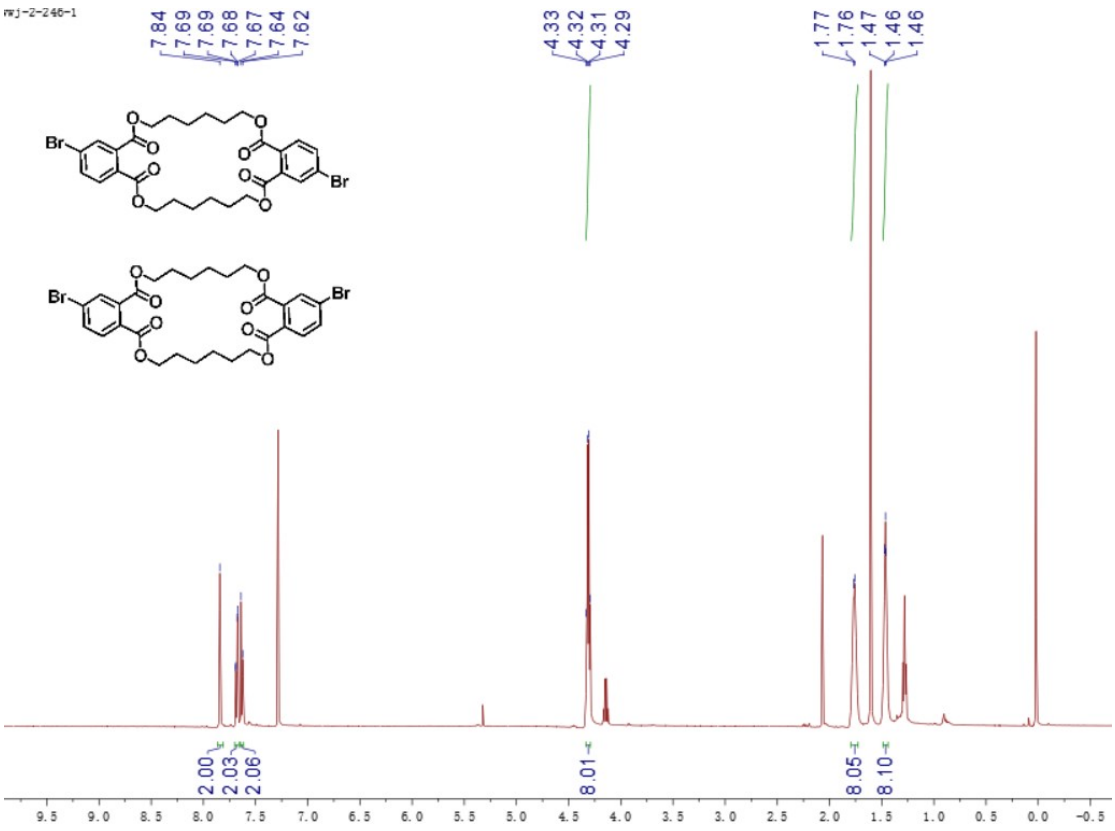


Figure S4. ^{1}H NMR spectrum of compound **2** ($CDCl_3$, 500 MHz).

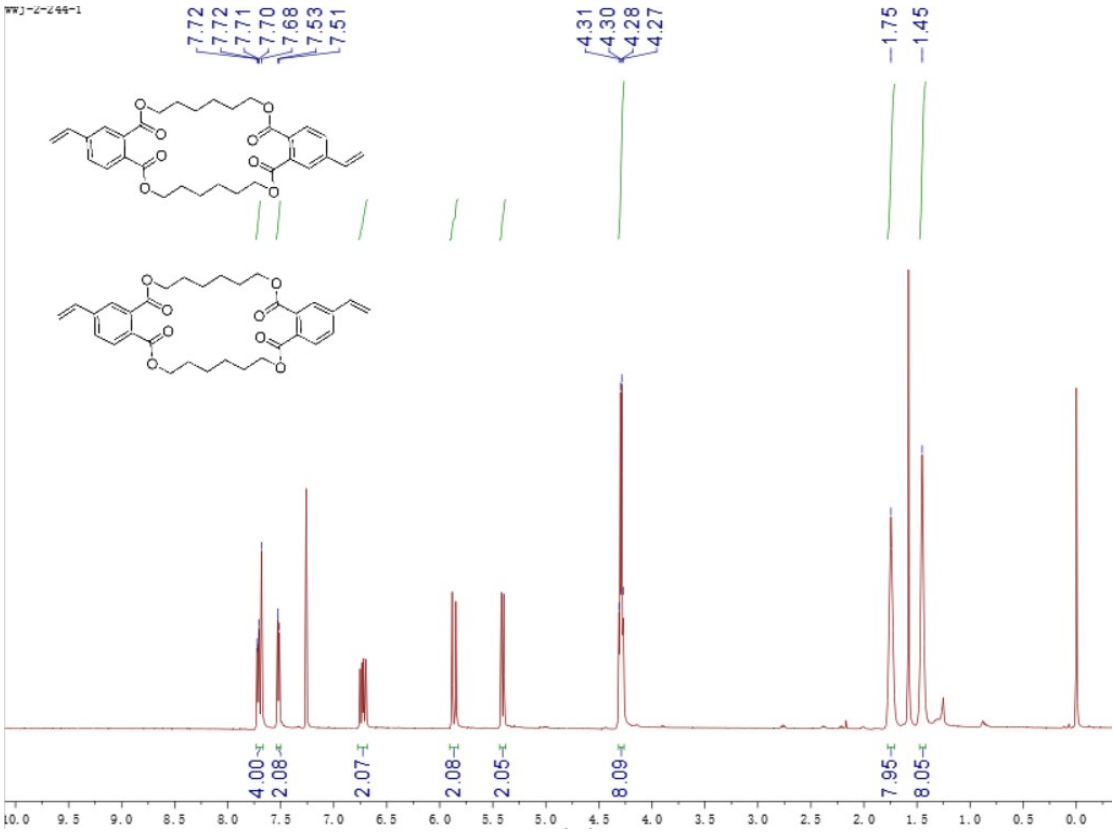


Figure S5. ^{1}H NMR spectrum of compound **DVMDE** ($CDCl_3$, 500 MHz).

2.2 Synthesis of the compound divinyl small cyclic diphthalate ester (DVSDE)

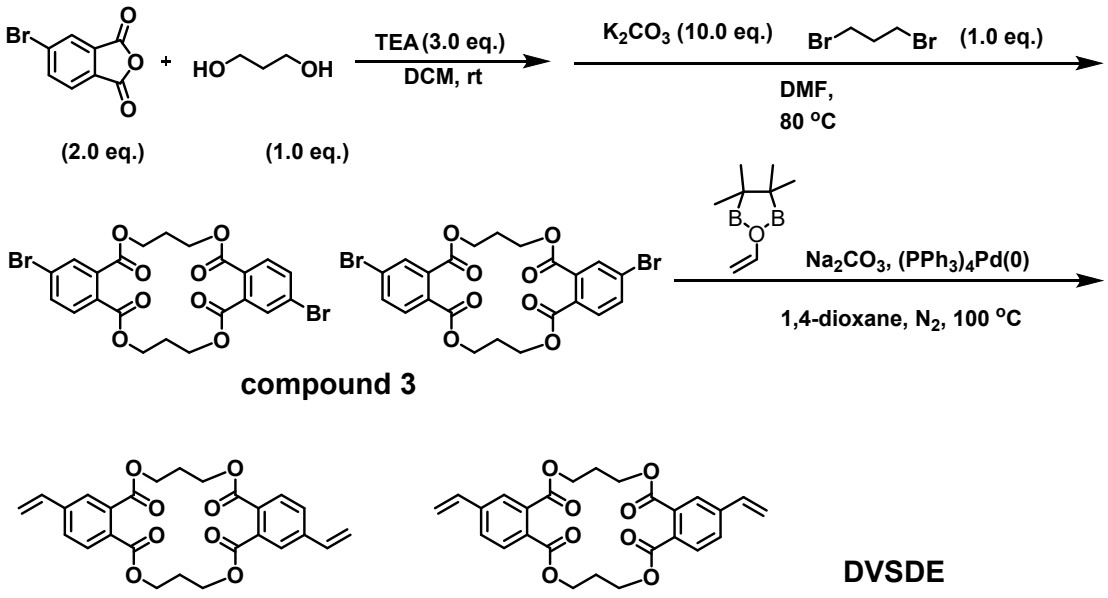


Figure S6. Synthesis of the compound **DVSDE**

The synthesis steps of divinyl small cyclic diphthalate ester (**DVSDE**) is referenced the

synthesis of **DVMDE**.

The product of compound **3** was a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) (Figure **S7**) δ 7.84 (m, 1H), 7.77 – 7.71 (m, 2H), 7.69 (m, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.58 – 7.53 (m, 2H), 4.56 – 4.12 (m, 8H), 2.28 – 2.04 (m, 4H). HRMS (ESI) ([M + Na]$^+$, $C_{22}H_{18}Br_2O_8Na$): calcd, 593.1821; found, 593.1822.

The product of compound **DVSDE** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) (Figure **S8**) δ 7.82 – 7.63 (m, 4H), 7.55 (d, J = 7.9 Hz, 2H), 6.71 (m, 2H), 5.89 (d, J = 17.6 Hz, 2H), 5.40 (t, J = 28.6 Hz, 2H), 4.42 (m, 8H), 2.27 – 2.02 (m, 4H). HRMS (ESI) ([M + Na]$^+$, $C_{26}H_{24}O_8Na$): calcd, 487.4611; found, 487.4609.

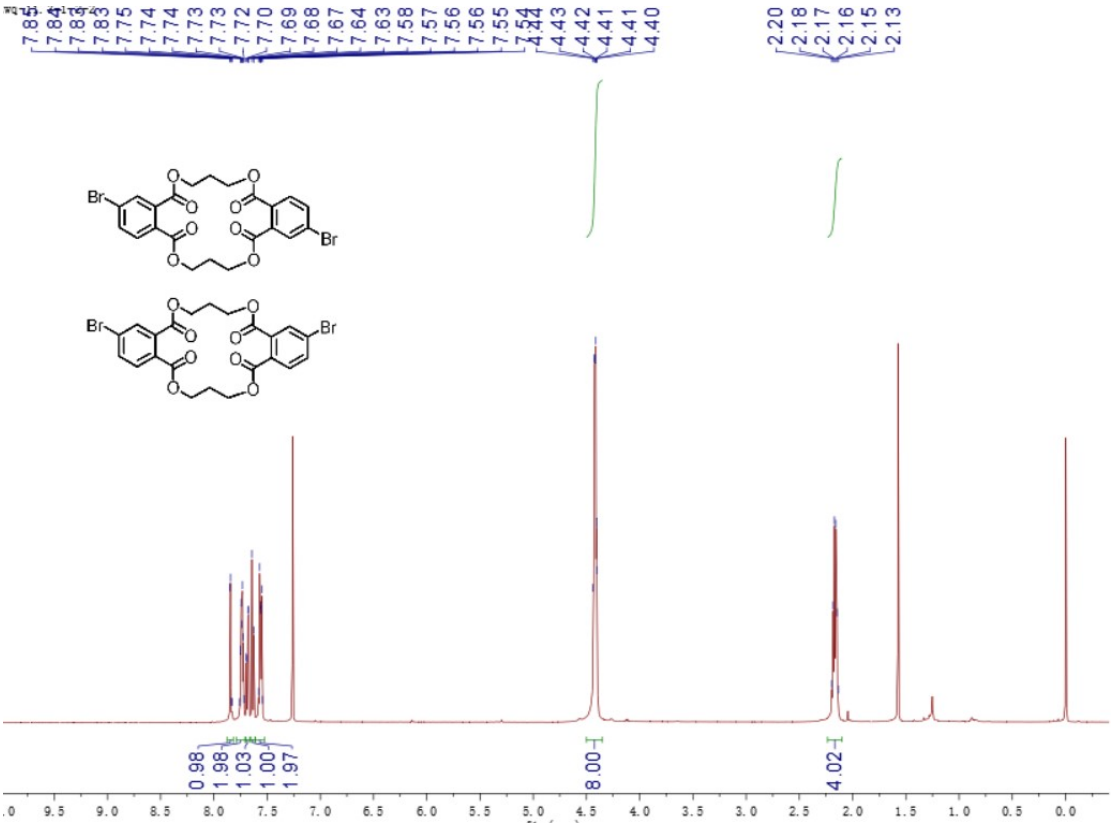


Figure S7. ^{1}H NMR spectrum of compound **3** ($CDCl_3$, 500 MHz).

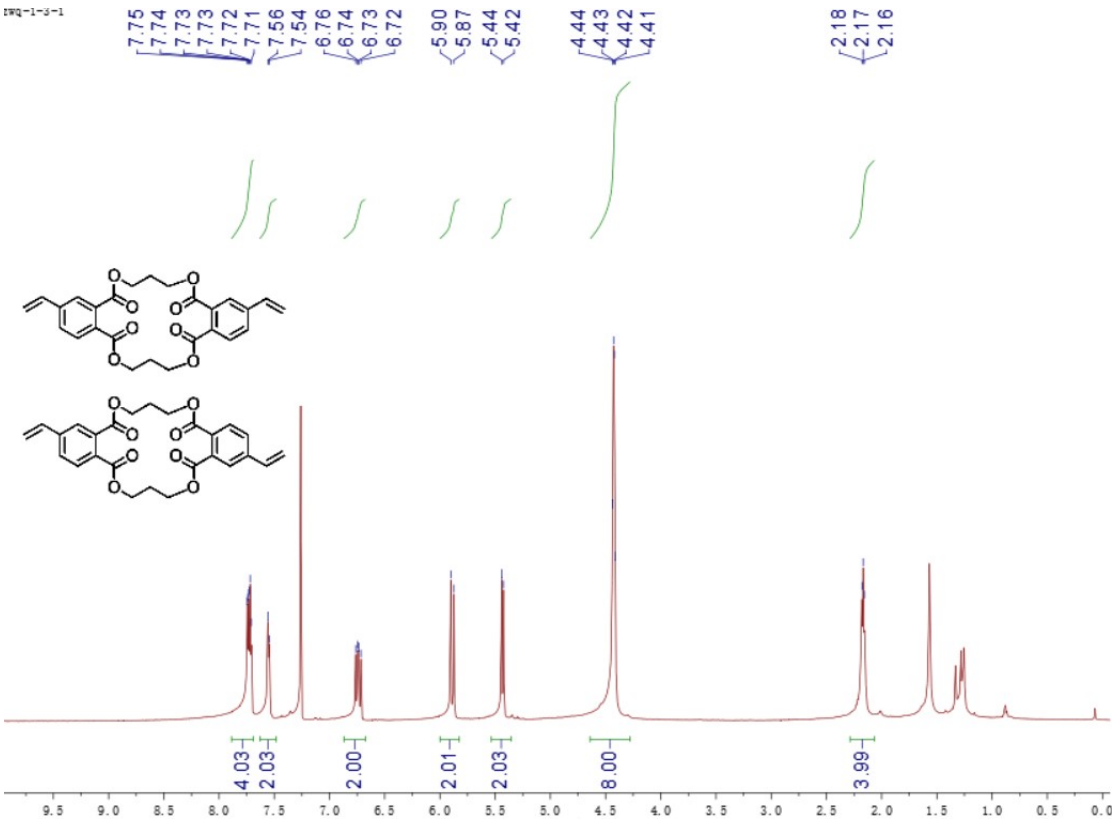


Figure S8. ^{1}H NMR spectrum of compound **DVSDE** ($CDCl_3$, 600 MHz).

2.3 Preparation of the Cross-Linked Composites (PMADs)

2.3.1 Preparation of the film of PMA.

Added MA (10 mmol, 860.9) and 5 mL1,4-dioxane in a 10 mL round bottom flask were mixture in room temperature with N_2 atmosphere. Then AIBN dissolved in 1,4-dioxane was added and the prepolymers was stirred at 70°C for 3 hours. Finally the mixture was poured in the PTFE mold and dried in an air oven at 80°C for 16 h. The final transparency film was PMA.

2.3.2 Preparation of the film of PMA/AA-2.4:1.

Added MA (7.2 mmol, 619.8 mg), AA (3.0 mmol, 216.2 mg) and 5 mL1,4-dioxane in a 10 mL round bottom flask were mixture in room temperature with N_2 atmosphere. Then AIBN dissolved in 1,4-dioxane was added and the prepolymers was stirred at

70°C for 3 hours. The final mixture was poured in the PTFE mold and dried in an air oven at 80°C for 16 h. The final transparency film was PMA/AA.

2.3.3 Preparation of the film of PMAD-2.4:1.

Added MA (7.2 mmol, 619.8 mg), AA (3.0 mmol, 216.2 mg), DVMDE (1 mol%, 56.0 mg) and 5 mL1,4-dioxane in a 10 mL round bottom flask were mixture in room temperature with N_2 atmosphere. Then AIBN dissolved in 1,4-dioxane was added and the prepolymers was stirred at 70°C for 3 hours. The final mixture was poured in the PTFE mold and dried in an air oven at 80°C for 16 h. The final transparency film was PMAD-2.4:1.

2.3.4 Preparation of the film of Control-DVSDE.

Added MA (7.2 mmol, 619.8 mg), AA (3.0 mmol, 216.2 mg), DVSDE (1 mol%, 47.4 mg) and 5 mL1,4-dioxane in a 10 mL round bottom flask were mixture in room temperature with N_2 atmosphere. Then AIBN dissolved in 1,4-dioxane was added and the prepolymers was stirred at 70°C for 3 hours. The final the mixture was poured in the PTFE mold and dried in an air oven at 80°C for 16 h. The final transparency film was Control-DVSDE.

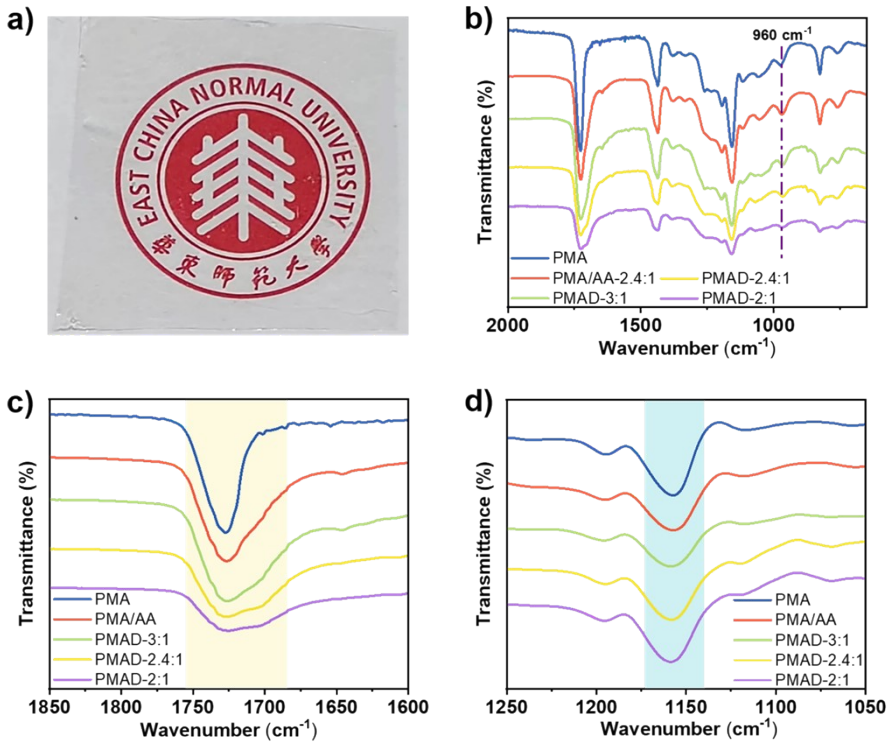


Figure S9. Characterization of non-/crosslinking polymers. a) Digital image of crosslinking polymer film of PMAD-2.4:1. It is highly transparent and stretchable. b-d) FT-IR spectra of non-/crosslinking polymers at room temperature. PMA: non-crosslinking polymers of MA; PMA/AA-2.4:1: non-crosslinking polymers of MA and AA; PMAD: crosslinking polymers of MA, AA and DVMDE with different molar ratios of MA to AA;

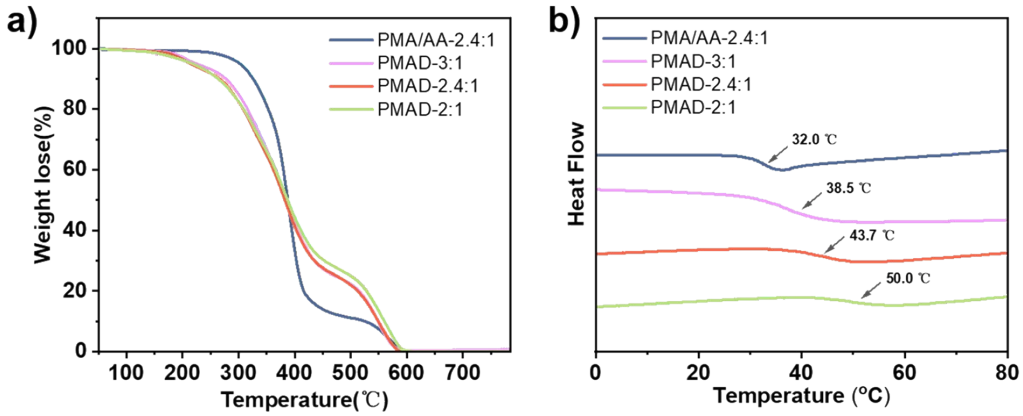


Figure S10. a) TGA curves of PMA/AA-2.4:1 and PMAD-x. b) DSC curves of PMA/AA-2.4:1 and PMAD-x.

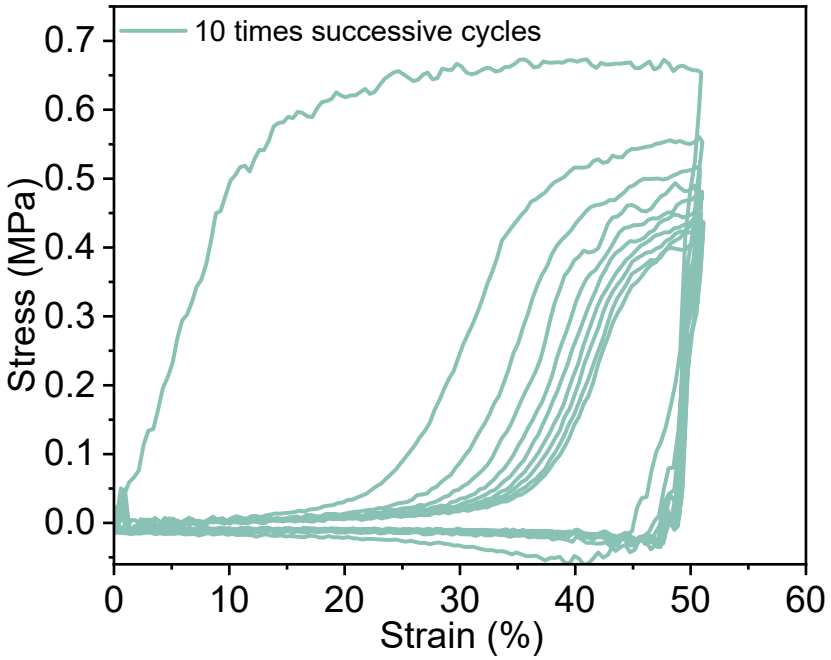


Figure S11. Cyclic tensile testing of PMAD-2.4:1.

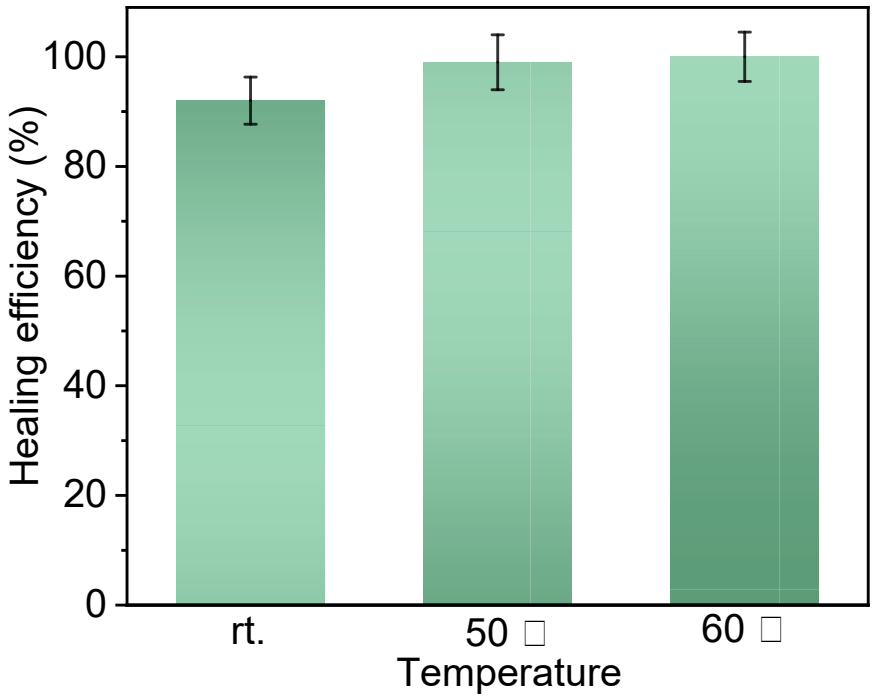


Figure S12. Healing temperature dependence of healing efficiency for PMDA-2.4:1.

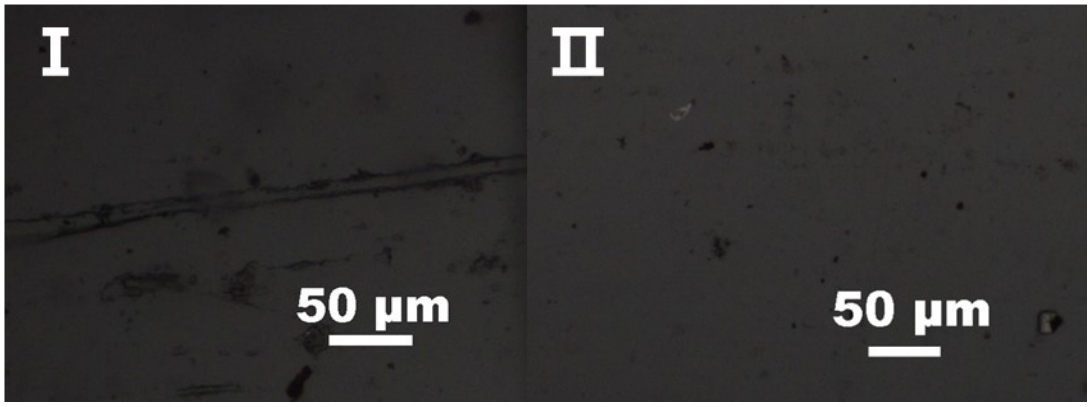


Figure S13. Optical microscopy images of artificially scratched PMAD-2.4:1 film and healing for 7 h at rt.

Table S1. Antibacterial ratio of PMAD-2.4:1, PMA/AA-2.4:1, Control-DVSDE.

Bacteria	Sa.6538	Sa.94004	Se.8187	Se.8188	Ec.8739	Ec25922
PMA/AA-OD630	0.312	0.365	0.341	0.423	0.455	0.411
PMVD-OD630	0.076	0.398	0.074	0.078	0.488	0.369
Control-OD630	0.454	0.586	0.563	0.581	0.447	0.399
Antibacterial ratio of PMA/AA	0.313	0.377	0.394	0.272	/	/
Antibacterial ratio of PMVD	0.833	0.321	0.869	0.866	/	7.5

Table S2. Antibacterial ratio of Control-DVSDE.

Bacteria	Sa.6538	Sa.94004	Se.8187	Se.8188	Ec.8739	Ec25922
Control-DVSDE	0.356	0.432	0.283	0.312	0.483	0.476
Control	0.584	0.676	0.468	0.442	0.455	0.524
Antibacterial ratio	39.04%	36.01%	39.53%	29.41%	/	9.16%

References

1. Y. Yoshimoto, M. Tanaka, M. Miyashita, M. Abdel-Wahab, A. M. A. Megaly, Y. Nakagawa, H. Miyagawa, *Journal of Natural Products* 2020**, 83** (2), 542-546.