Supporting Information for

Photo-Curable Hyperbranched Polymer Medical Glue for Water-Resistant Bonding

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Synthesis of 2-(acryloyloxy) ethyl methacrylate

Acrylic acid (144.16 g, 2 mol), phloroglucinol (0.260 g, 20 mmol), hydroxyethyl methacrylate (130.14 g, 1 mmol) and p-toluenesulfonic acid (5.17 g, 30 mmol) were dissolved in toluene (200 mL), then was heated to 90 ºC for 3 h. Subsequently, the reaction mixture was washed 6 times with deionized water to remove excess reactant, and then dried by anhydrous sodium sulfate. The residue was further purified by a neutral alumina column and then the organic solvent was thoroughly evaporated to afford colorless liquid (125.31 g, 68.6% yield).

Absolute molecular weight and its distribution:

The detailed polymer parameters of HBPTE were measured using a multi-angle laser light scattering system (DAWN HELEOS II System, Wyatt Technology Corporation) combine with a gel permeation chromatogram (GPC, Waters 1515-2414-2707, Agilent organic column, PMMA standard, mixed-C column). The DMF added with 10 mmol·L^{-1} of LiBr was used as the eluent at a flow rate of 0.5 mL min^{-1}. First, a series of hyperbranched polymers solution with gradient concentration (5 mg/mL, 10 mg / mL, 15 mg/mL, 20 mg/mL and 25 mg/mL) were measured though a laser detector (120 mW, λ = 664 nm, WYATT-1486-H2, DAWN HELEOS) to obtain the d_n/d_c (specific refractive index increase). Then the intrinsic viscosity of the polymer was detected with a viscosity detector. The original data is processed with Astra VI software, the absolute weight average molecular weight of the sample was fitted by d_n/d_c, and the MHS index (α) was fitted by the intrinsic viscosity and absolute weight average molecular weight.

Rheological properties:

The viscosity, elastic modulus and loss modulus of HBPTE was determined using a

Discovery Hybrid Rheometer (DHR-2, TA Instruments, DE, USA) equipped with a parallel plate (8 mm diameter). The gap value was set to 100 μm at 25 °C. Before measurement of storage modulus (G′) and loss modulus (G″), the linear viscoelastic region (LVR) was determined after a strain-sweep test between 0.1% and 20% at a constant frequency of 1 Hz. The LVR was concluded to be around 1% strain, since G′ and G″ were linearly dependent with strain around that value. Next, G′ and G″ was measured during a dynamic frequency-sweep test in a range of frequencies between 0.1 Hz and 1 Hz with a constant strain of 1% at 25 °C. Then, polymer viscosity was measured as a function of shear rate between 0.1 and 100 s^{-1}.

***Transmittance test*:**

HBPTE, PEGDMA and 0.2 wt% Irgacure 2959 was mixed in a quartz cuvette, and then was cured for 1 minute. The transmittance was measured using ultraviolet-visible spectroscopy spectrophotometer (UV-vis, TU-1901) in a range of wavelength between 400 nm and 900 nm with an empty cuvette as a reference.

Storage stability:

Taking HBPTE1-0.2 as an example to evaluate the storage stability of glue by a vial tilting method. The vial contained about 2 mL of glue was placed in a dark environment at 25 °C, and the time when flow is not observed after tilting was recorded.

Lap shear adhesive test:

The HBPTE-glue was applied to a glass slide in an area of 2.50 cm × 2 cm. Then, another glass slide was used to overlap over the area with glue applied. Subsequently, the lap joints were cured using UV light irradiation of 10 $J \cdot cm^{-2}$ and then immersed into a PBS solution at 37 °C for two weeks. To prevent breakage of the brittle glass slide with tension applied, two

iron steel rods were coated with cyanoacrylate glue and superimposed on the slide. Afterwards, lap shear tests were carried out using a universal testing machine (ITW 5967X, USA) equipped with a 500 N load cell at a tensile speed of 5 mm/min. The results were reported as average and standard deviations of five measurements.

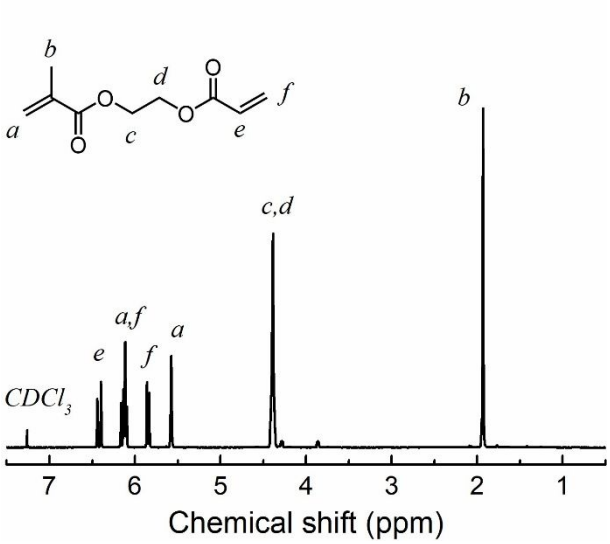

Figure S1: ^{1}H NMR spectrum recorded of 2-(acryloyloxy) ethyl methacrylate in $CDCl_3$.

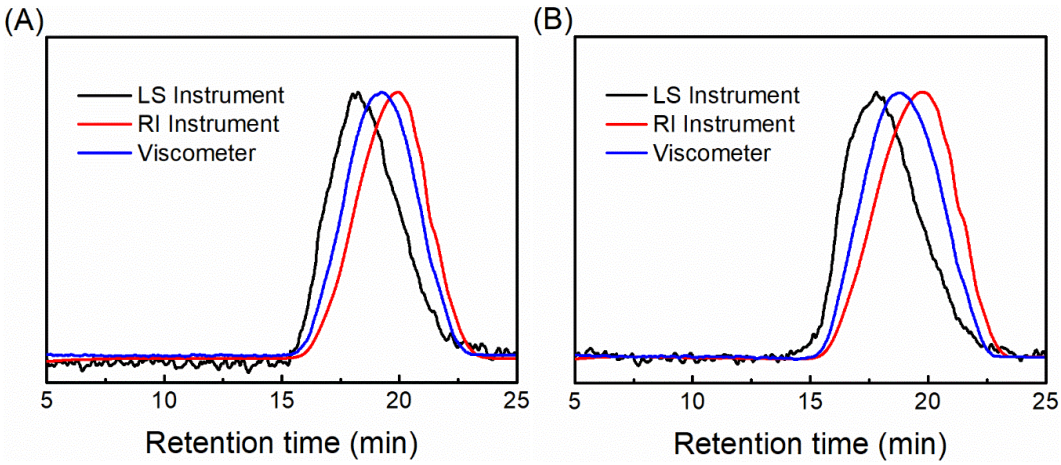

Figure S2: The molecular weight distribution curves of HBPTE1(A) and HBPTE12 (B) recorded by light scattering (LS) detector, refractive index (RI) and viscometer, respectively.

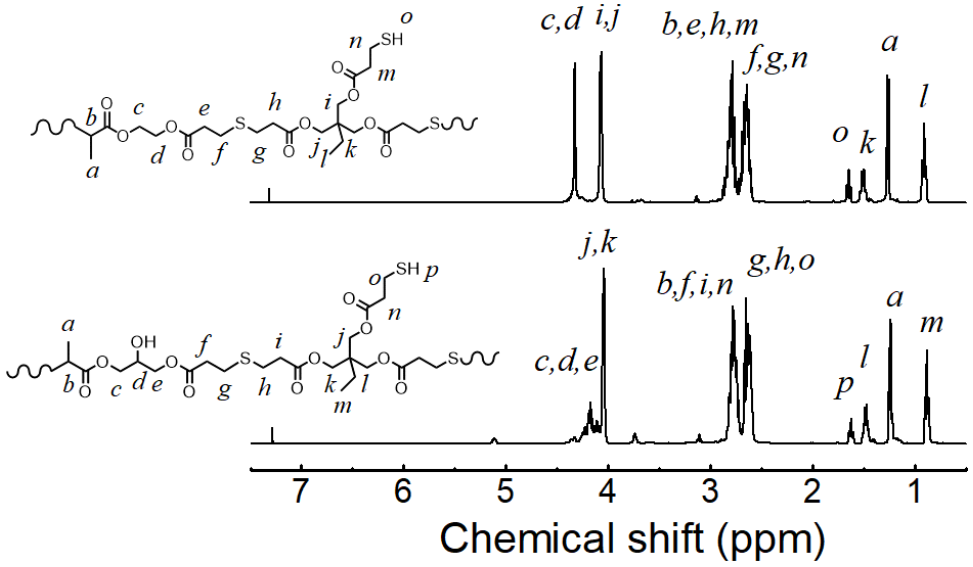

Figure S3: ^{1}H NMR spectra recorded of HBPTE in $CDCl_3$.

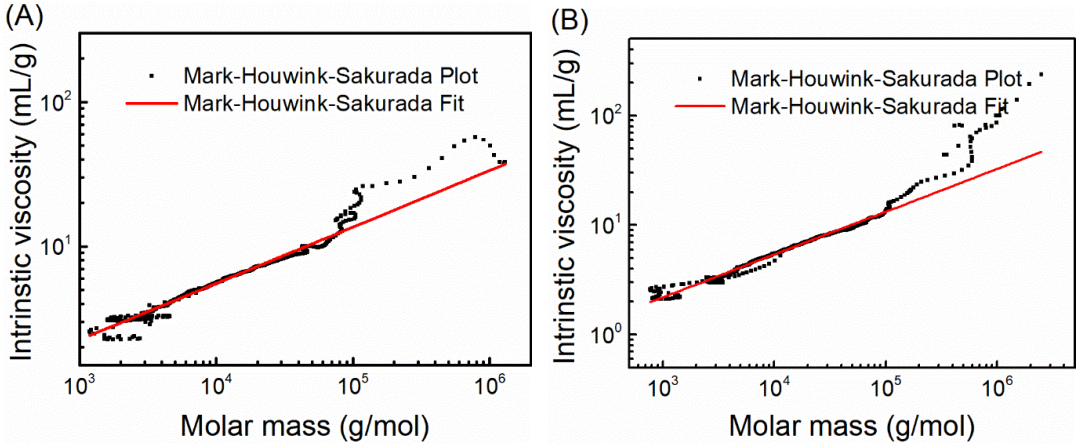

Figure S4: The Mark-Houwink-Sakurada plot and fit line of HBPTE1(A) and HBPTE12 (B).

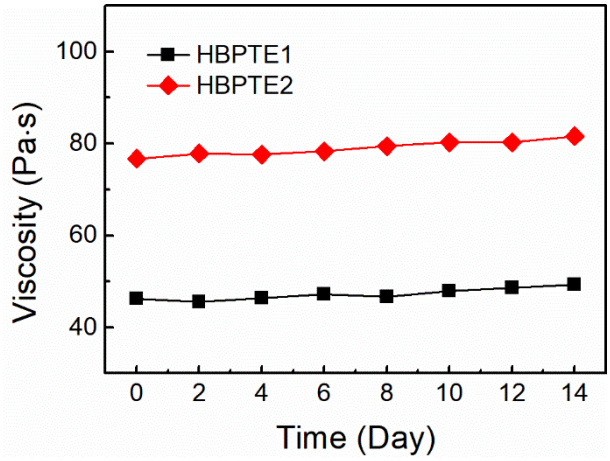

Figure S5: The viscosity change of HBPTE as a function of storage time at room

temperature.

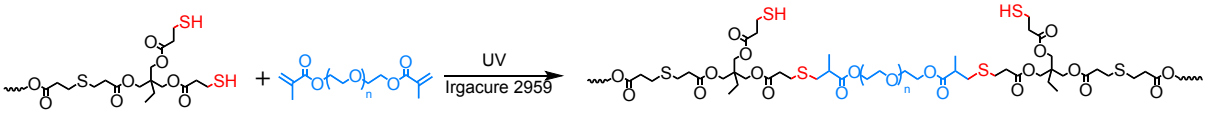

Figure S6: Schematic illustration of photo-crosslinking of HBPTE glue.

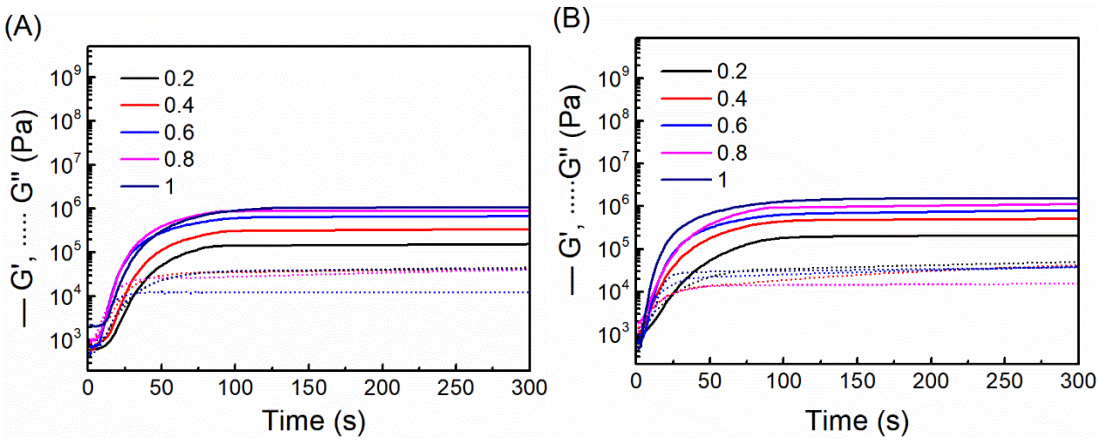

Figure S7: Real time rheology profile of HBPTE1 glue (A) and of HBPTE2 glue (B) at a UV (365 nm) energy of 20 mW/cm^2.

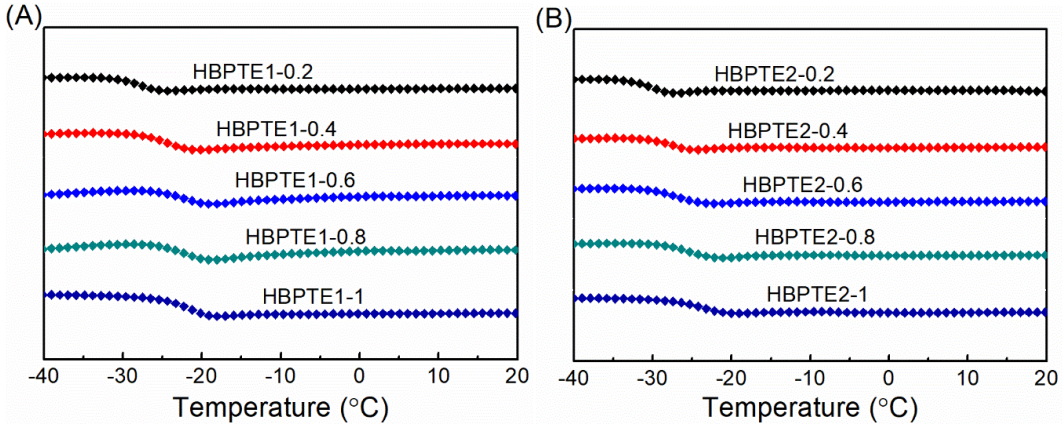

Figure S8: DSC curve of cured HBPTE1 glue (A) and HBPTE2 glue (B).

Figure S9: Storage stability test of HBPTE1-0.2 via vial tilting method under dark environment at room temperature.

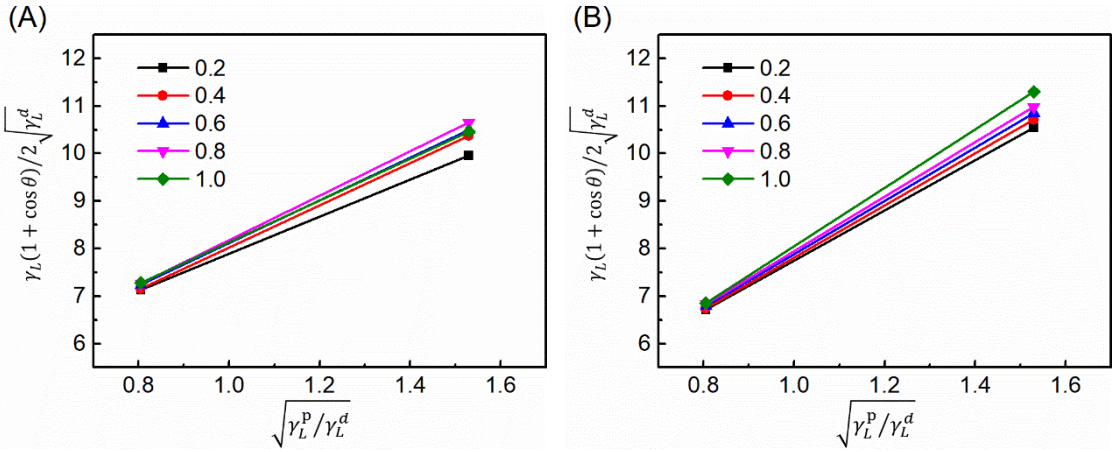

Figure S10: Surface energy fitting plot of HBPTE1 glue (A) and HBPTE1 glue (B) according to the contact angles made by ethylene glycol and water.

Table S1 Summary of the surface energy of HBPTE1 and HBPTE2 glue.

Sample	HBPTE1 glue					HBPTE2 glue				
	0.2	0.4	0.6	0.8	1	0.2	0.4	0.6	0.8	1
γ^d	15.85	12.86	13.14	12.21	11.64	6.04	5.37	5.12	4.93	3.64
γ^p	15.27	19.69	20.21	21.91	23.09	27.91	30.16	31.56	32.79	37.7
γ	31.12	32.55	33.35	34.12	34.73	33.96	35.53	36.68	37.72	41.34

Polar component (γ^d) and dispersion component (γ^p) of surface energy of HBPTE glue.

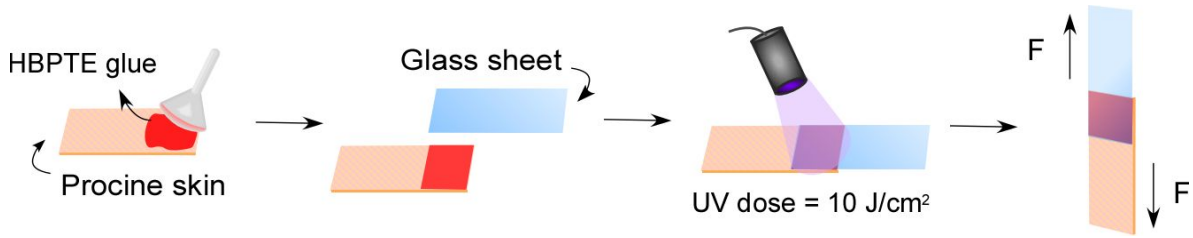

Figure S11: Schematic representation of the lap-shear joints for the porcine adhesive test.

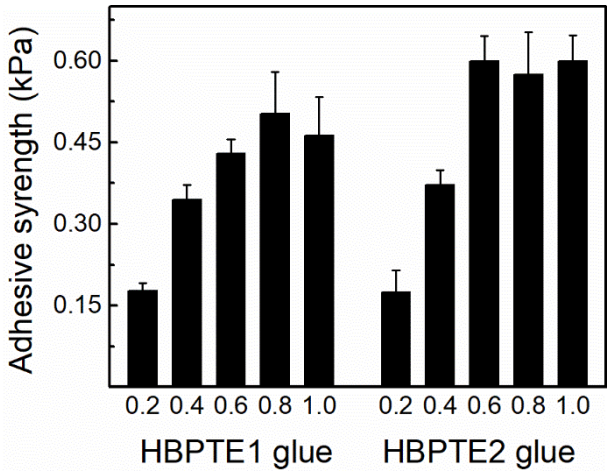

Figure S12: Lap-shear strength of HBPTE glue on glass sheet.

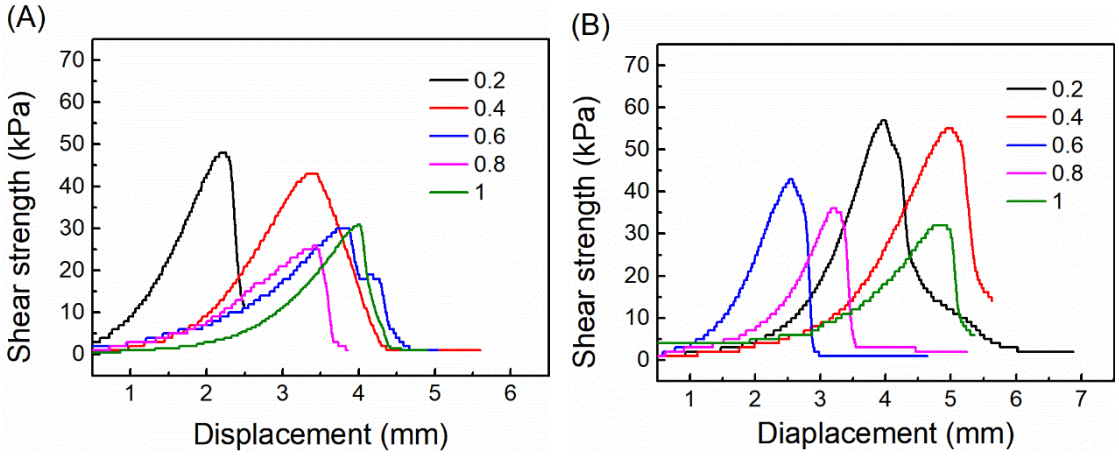

Figure S13: Lap shear bonding curve of the porcine skin sample bonded by HBPTE1 glue (A) and HBPTE2 glue (B).

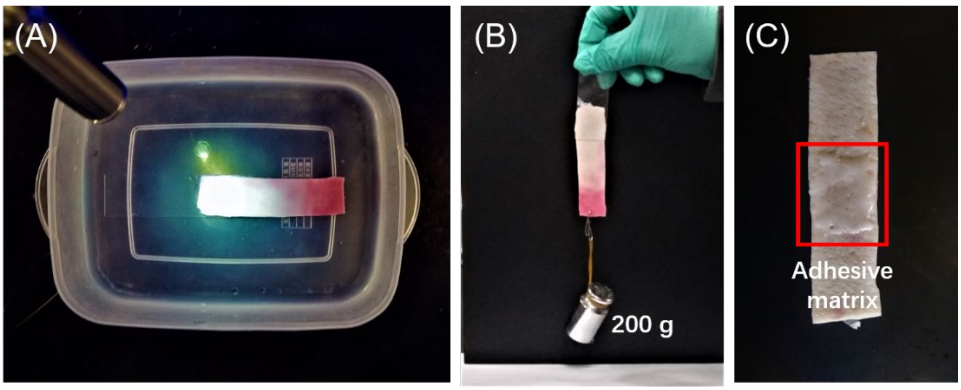

Figure S14: (A) The photo image of underwater adhesion test of HBPTE1-0.2 in PBS (pH = 7.4). (B) The HBPTE1-0.2 bonded porcine can lift a 200 g weight. (C) The photo image depicting HBPTE1-0.2 still adhered on porcine skin after soaking in water for two weeks.

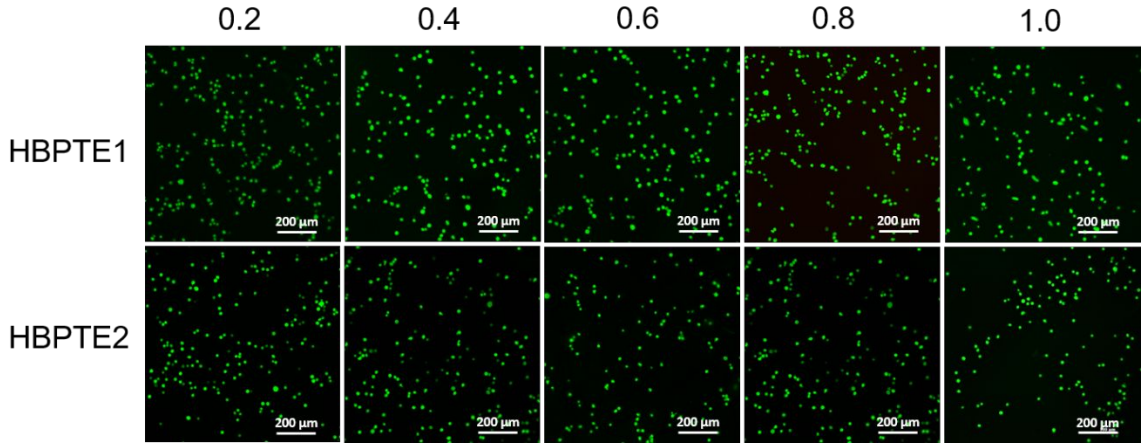

Figure S15: Live/dead staining confocal images of L929 cell present on cured HBPTE glue after 24 h.

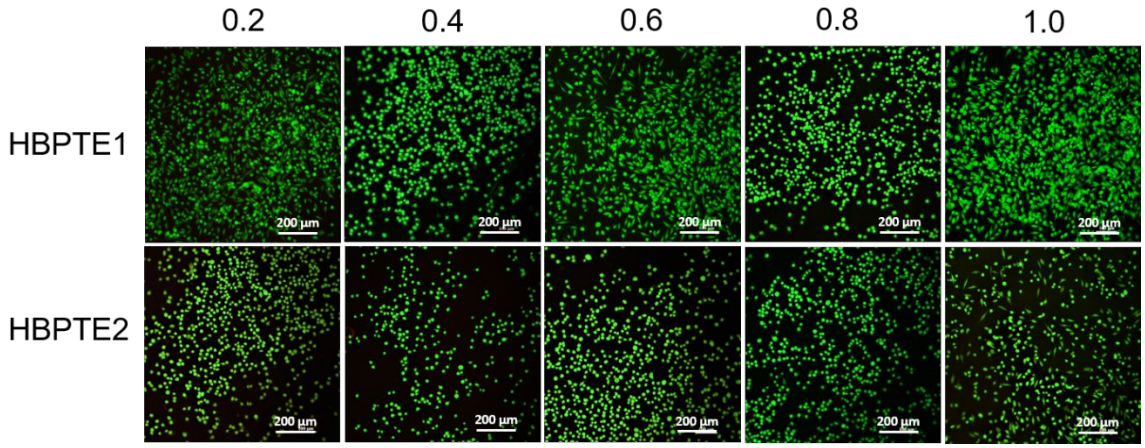

Figure S16: Live/dead staining confocal images of L929 cell present on cured HBPTE glue

after 48 h.

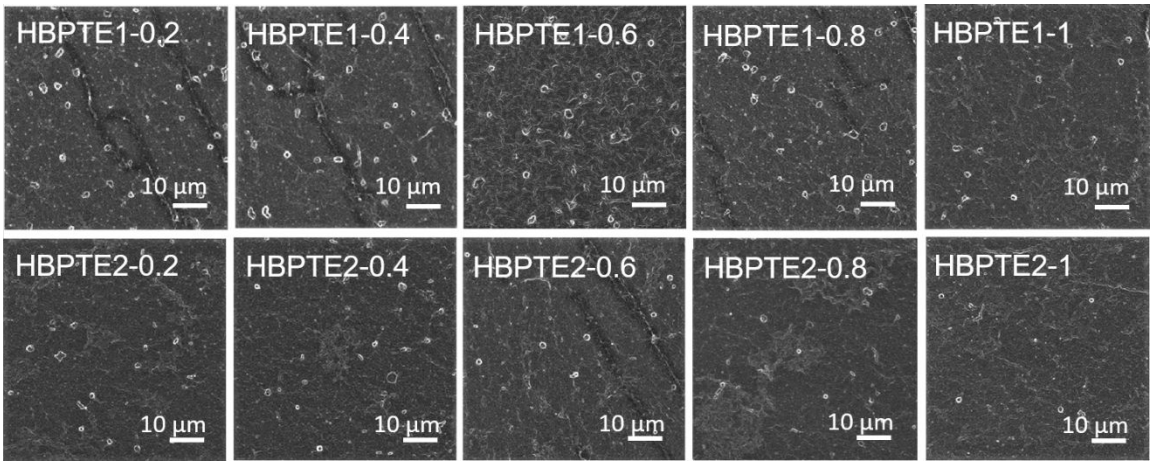

Figure S17: SEM images of adhered platelets on cured HBPTE glue.