Supporting Information

Atom-Economic Molecular Design of Vanillin-Based Tetraene for Tunable Polyester via Thiol-ene Click Polymerization

Zijun Gao,[a,b] *Qin Chen* *[a,b], and *Haibo Xie* *[a,b]

[a]Department of Polymeric Materials & Engineering, College of Materials & Metallurgy, Guizhou University, Huaxi District, Guiyang 550025, P.R. China.

[b]Technology Innovation Center for High-Efficiency Utilization of Bamboo-Based Biomass in Guizhou Province, Guiyang 550025, China

E-mail: qchen6@gzu.edu.cn; hbxie@gzu.edu.cn

1. Materials

Vanillin (99%), allyl bromide, sodium hydride, trimethylolpropane tris(3-mercaptopropionate) (TPTMP), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Aladdin Company (Shanghai, China). Ethylene glycol bis(3-mercaptopropionate) (EGMP) was purchased from MACKLIN Company.

2. Characterizations

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZ-400S/L1 spectrometer (400 MHz) using DMSO-d_6 or $CDCl_3$ with tetramethylsilane (TMS, $\delta = 0$ ppm) as the internal reference.

Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a Nicolet iS50 FT-IR instrument (Thermo Nicolet Corporation, America) under attenuated total reflectance (ATR) mode with the following parameters: 32 scans from 4000 to 550 cm^{-1}.

Differential scanning calorimetry (DSC) thermograms were measured by TA Q2000 instrument. The glass transition temperature (T_g) of the bio-based polyesters were obtained from second heating cycle with a heating rate of 10 ^{o}C/min from -20 ^{o}C to 120 ^{o}C under nitrogen atmosphere.

The thermomechanical properties of the bio-based polyesters were characterized using a dynamic mechanical analyzer (DMA Q800, TA Instruments, USA). Rectangular specimens (30 mm × 6 mm × 0.3 mm) were analyzed in film tension mode with the following parameters: temperature ramp from −50 to 100 ^{o}C at 3 ^{o}C min^{-1}, frequency of 1 Hz, under nitrogen purge.

The thermal stability was evaluated using a thermogravimetric analyzer (209F1 TG, Netzsch, Germany). Measurements were performed under a nitrogen atmosphere with a heating rate of 10 ^{o}C min^{-1} from ambient temperature to 800 ^{o}C.

Tensile tests were conducted on an electronic universal testing machine (TSE104B, Shenzhen, China) at a crosshead speed of 10 mm min^{-1} under ambient conditions.

The transparency properties of the bio-based polyester films were acquired using a UV-visible spectrophotometer (UV-2700, Shimadzu, Japan). Measurements were performed in the wavelength range of 200 – 800 nm, using air as the reference.

The swelling degree and gel content of the bio-based polyesters were determined gravimetrically. Samples (around 30 mg, M1) were immersed in DMF and THF for 48 h at ambient temperature. The swollen mass (M2) was recorded after blotting excess solvent. Subsequently, samples were dried at 70 °C for 24 h under vacuum to obtain the residual mass (M3). The swelling degree (SD) and gel content (GC) are calculated as follows:

$$SD = \frac{M2 - M1}{M1} \times 100\%$$

$$GC = \frac{M3}{M1} \times 100\%$$

3. Experimental protocols

3.1 Synthesis of 4-(allyloxy)-3-methoxybenzaldehyde (AM)

Vanillin (100 mmol, 1.0 equiv.), potassium carbonate (110 mmol, 1.1 equiv.), and anhydrous ethanol (100 mL) were charged into a 250 mL two-necked round-bottom flask equipped with a magnetic stirrer. The reaction mixture was heated to 40 °C in an oil bath with continuous stirring until the vanillin completely dissolved. Then, allyl bromide (110 mmol, 1.1 equiv.) was added dropwise, and the mixture was refluxed at 80 °C for 24 hours. After cooling to ambient temperature, the inorganic salts were removed by vacuum filtration. The filtrate was concentrated under reduced pressure using a rotary evaporator. The residue was dissolved in ethyl acetate (200 mL) and washed with deionized

water (3 × 50 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. Final purification was achieved by flash column chromatography on silica gel (ethyl acetate /petroleum ether = 1/3). Yield: 96%. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.81 (s, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.38 (s, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.10 – 6.01 (m, 1H), 5.41 (ddd, J = 13.9 Hz, 11.7 Hz, 1.3 Hz, 2H), 4.67 (dt, J = 5.2, 1.2 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 191.0, 153.5, 149.9, 132.3, 130.2, 126.7, 118.9, 111.9, 109.2, 69.8, 56.1.

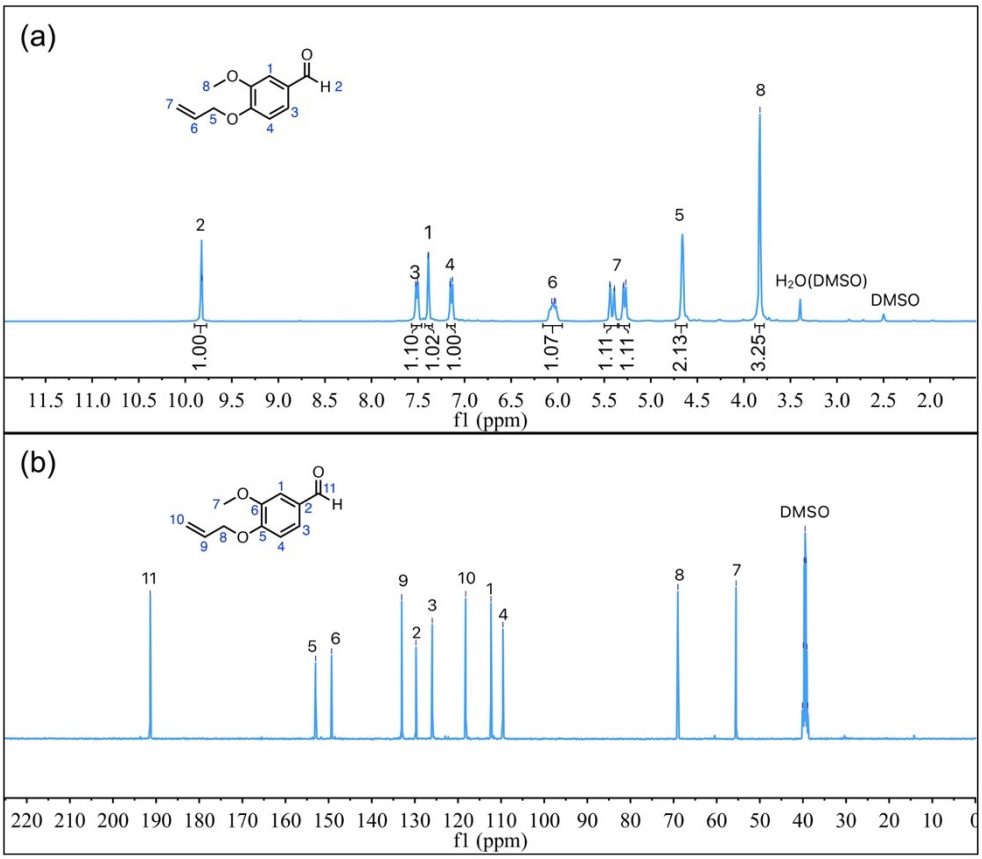

Figure S1. ^{1}H NMR and ^{13}C NMR spectra of **AM**.

3.2 Synthesis of 3-allyl-4-hydroxy-5-methoxybenzaldehyde (AHM)

AM (10 mmol, 1.0 equiv.) was added to a 50 mL two-necked round-bottom flask. The mixture was immersed in a 200 °C oil bath and stirred magnetically for 3.5 hours under nitrogen atmosphere.

After the reaction, the crude product was purified via recrystallization from n-hexane to afford the target compound. **AHM** was obtained as a yellow solid, yield: 78%. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 9.80 (s, 1H), 7.31 (s, 2H), 6.33 (s, 1H), 6.00 (dd, J = 17.4, 9.6 Hz, 1H), 5.19 – 5.02 (m, 2H), 3.95 (s, 3H), 3.46 (d, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 149.5, 147.0, 135.6, 129.1, 128.2, 126.1, 116.5, 107.0, 56.3, 33.6.

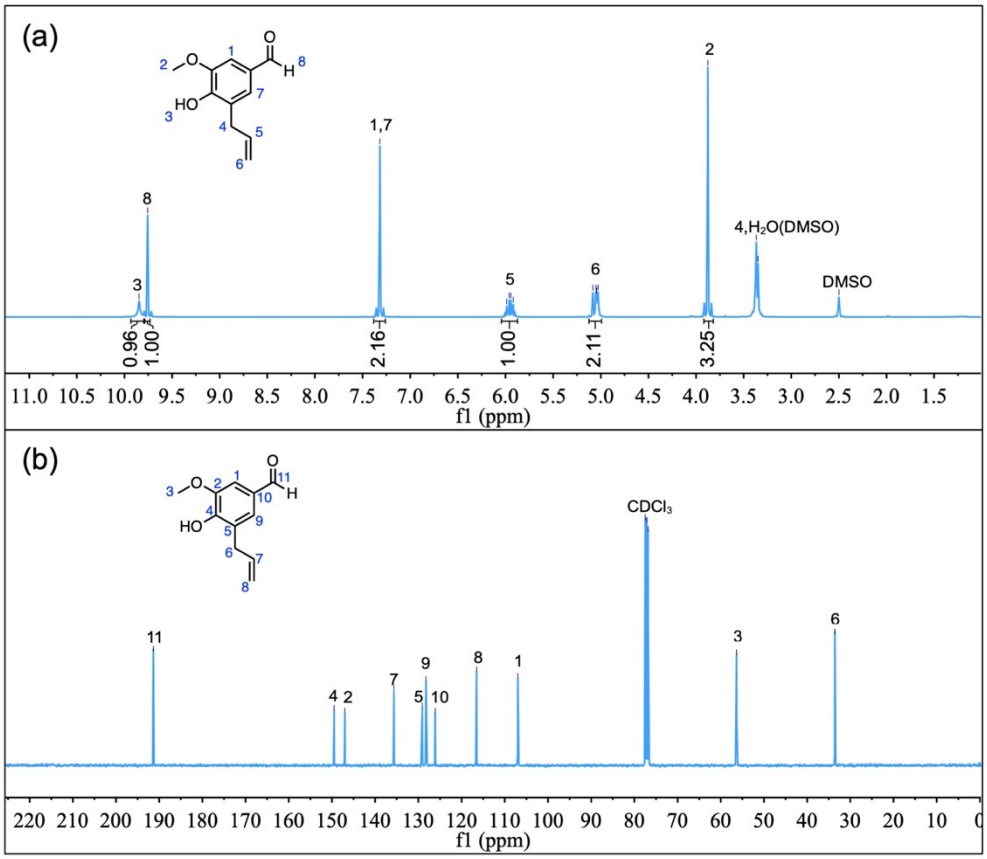

Figure S2. ^{1}H NMR and ^{13}C NMR spectra of **AHM**.

3.3 Synthesis of 3-allyl-4-(allyloxy)-5-methoxybenzaldehyde (AAM)

AAM was prepared from the **AHM** following the identical synthetic procedure as described for **AM**. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/6) to obtain yellow liquid, yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.87 (s, 1H),

7.32 (s, 2H), 6.13 – 5.90 (m, 2H), 5.42 – 5.31 (m, 1H), 5.24 (dd, J = 10.4, 1.3 Hz, 1H), 5.13 – 5.04 (m, 2H), 4.59 (d, J = 5.9 Hz, 2H), 3.91 (s, 3H), 3.47 (d, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 186.8, 148.6, 146.6, 131.6, 129.9, 129.1, 127.6, 121.9, 113.3, 111.8, 104.2, 69.2, 51.2, 29.5.

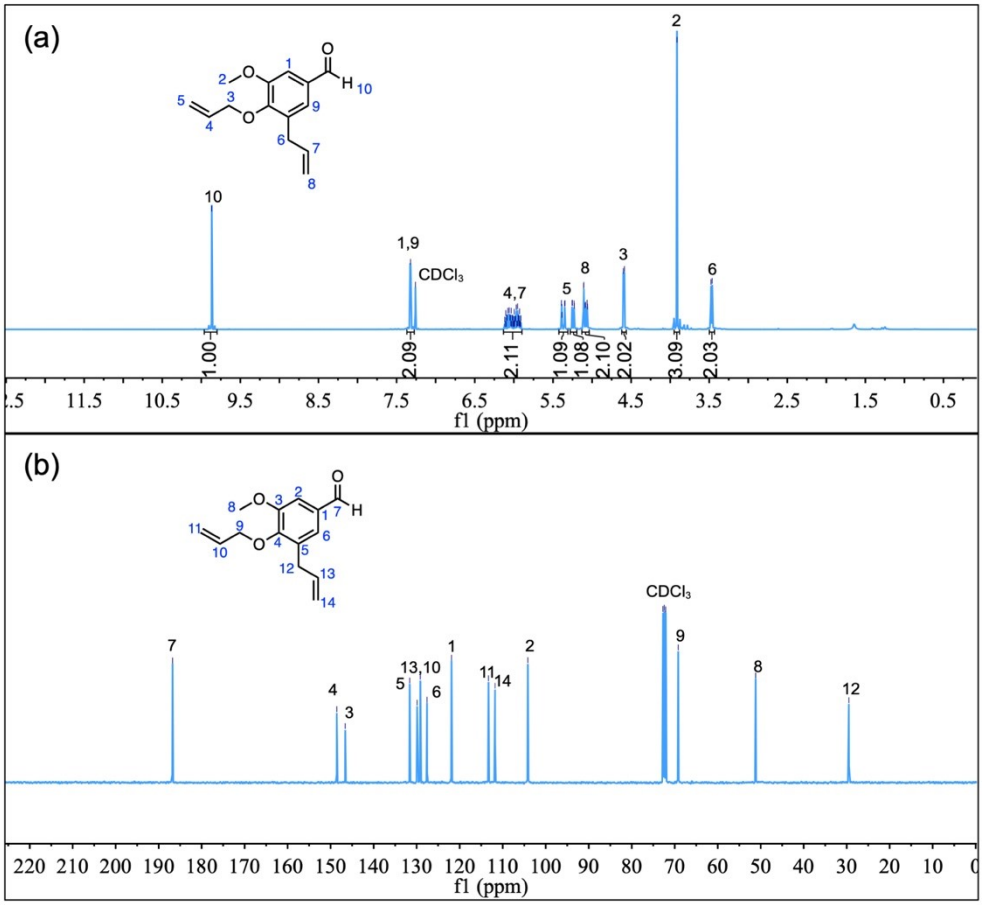

Figure S3. ^{1}H NMR and ^{13}C NMR spectra of **AAM**.

3.4 Synthesis of 3-allyl-4-(allyloxy)-5-methoxybenzyl 3-allyl-4-(allyloxy)-5-methoxybenzoate (TVE)

Sodium hydride (60% dispersion in mineral oil, 1 mmol, 10 mol%) was added to **AAM** (10 mmol) in a Schlenk-flask at 110 °C. The mixture was stirred under reduced pressure (20 mbar) for 24 h. After the reaction, the mixture was diluted with water (30 mL), and the aqueous phase was extracted with

ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/15). A yellow clear liquid was obtained, yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.55 (s, 1H), 7.49 (s, 1H), 6.87 (s, 2H), 6.18 – 5.87 (m, 4H), 5.43 – 5.32 (m, 2H), 5.26 (s, 2H), 5.22 (dt, J = 10.1, 1.3 Hz, 2H), 5.13 – 4.99 (m, 4H), 4.55 (dt, J = 5.9, 1.4 Hz, 2H), 4.52 – 4.46 (m, 2H), 3.87 (d, J = 12.4 Hz, 6H), 3.43 (d, J = 6.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 165.2, 153.1, 146.3, 137.4, 134.9, 134.7, 134.5, 132.3, 126.0, 124.6, 122.5, 118.1, 116.5, 112.1, 111.0, 74.3, 67.2, 56.4, 34.8.

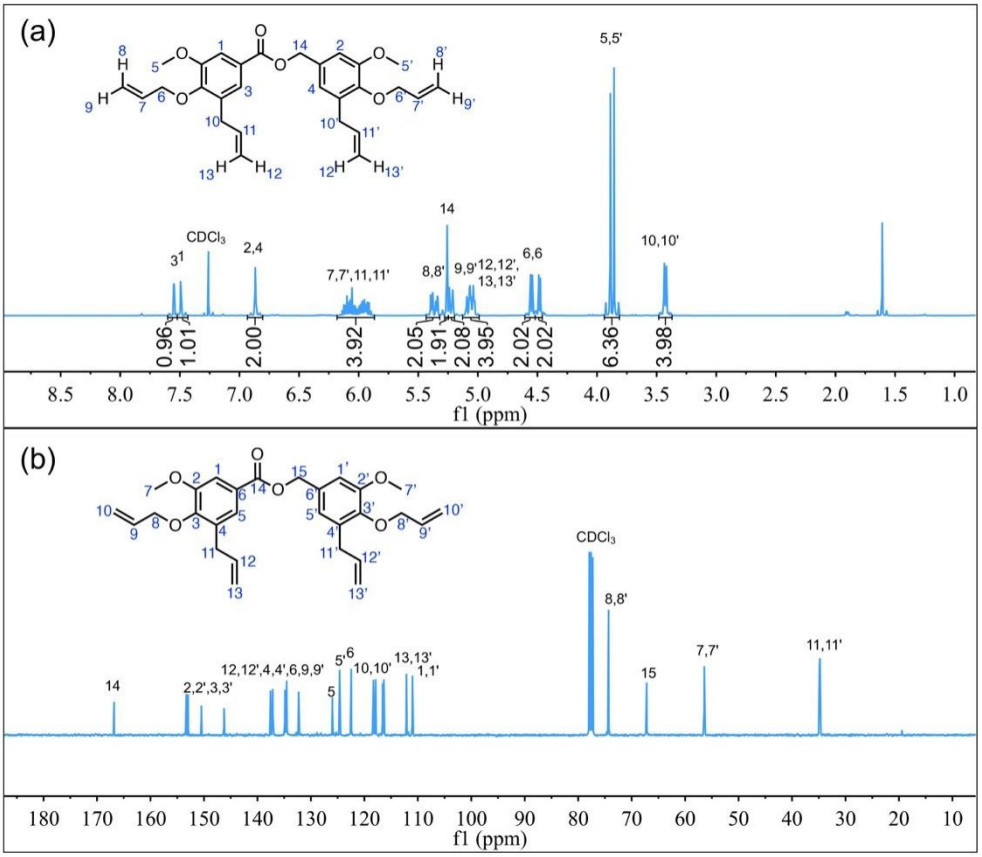

Figure S4. ^{1}H NMR and ^{13}C NMR spectra of **TVE**.

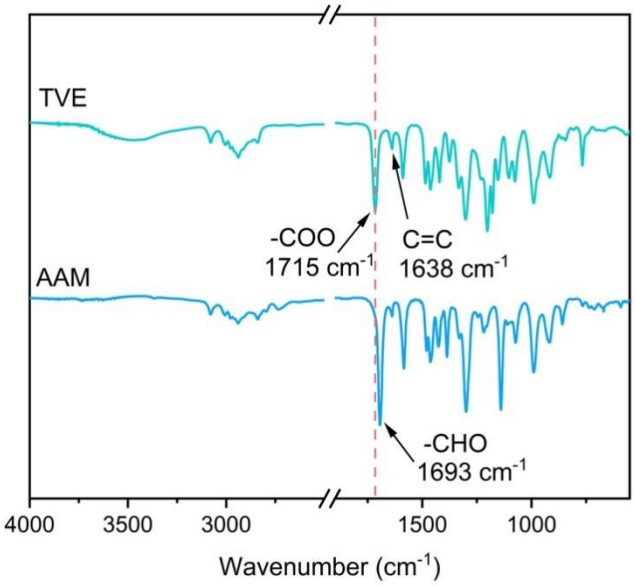

Figure S5. Comparison of FT-IR spectra of **AAM** and **TVE**.

3.5 Preparation of the thiol-ene polyester networks

TVE, EGMP (1.0 equiv. C=C/-SH), and the DMPA (1 wt% of the total weight of **TVE** and EGMP) were mixed thoroughly at 50 °C for 10 min to obtain a clear liquid. The required mass of each thiol monomer was calculated based on a 1:1 molar ratio of C=C to -SH functional groups, using the equation:

$$Mass\ of\ thiol = \frac{n_{TVE} \times 4 \times M_{thiol}}{Functionality\ of\ thiol}$$

Where n_{TVE} is Moles of **TVE**, M_{thiol} is the molecular weight of the thiol monomer.

The liquid was cast into a culture and cured under UV irradiation with 365 nm light for 10 min, followed by thermal post-curing at 120 °C for 30 min to yield the crosslinked network, coded as **TVE-2SH**. Similarly, TPTMP and PETMP were employed to prepare **TVE-3SH** and **TVE-4SH** networks.

Table S1. DSC and DMA results of **TVE-SH** films.

Sample	T_{gDSC} (°C)	T_{gDMA} (°C)	E' (25 °C) (MPa)	E' (T_{gDMA}+40 °C) (MPa)	υ_e (mol m^{-3})
TVE-2SH	0.1	6.4	6.4	6.5	815.5
TVE-3SH	13.5	26.4	79.6	8.6	1015.5
TVE-4SH	26.2	36.8	536.4	11.6	1351.9

Table S2. Thermogravimetric parameters of **TVE-SH** networks.

Sample	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	T_{dmax} (°C)	Char yield (%)
TVE-2SH	319.5	334.1	362.7	14.1
TVE-3SH	333.4	343.7	354.5	13.8
TVE-4SH	333.8	344.3	357.7	18.9

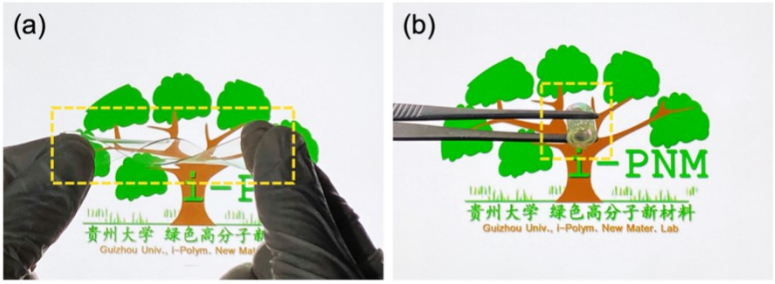

Figure S6. Digital photos of **TVE-3SH** (a) after twisting, and (b) after curling.

Table S3. Tensile properties of **TVE-SH** networks.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Toughness (MJ/m^3)
TVE-2SH	1.9±0.2	50.6±0.9	4.8±0.2	0.4±0.1
TVE-3SH	6.2±0.7	79.7±8.1	7.8±0.0	2.5±0.5
TVE-4SH	17.1±1.1	60.9±2.3	310.4±6.0	7.3±0.7

Table S4. Swelling degree and gel content of **TVE-SH** networks.

Sample	DMF		THF	
	SD (%)	GC (%)	SD (%)	GC (%)
TVE-2SH	58.0	99.5	68.8	99.8
TVE-3SH	44.0	99.1	52.4	99.0
TVE-4SH	35.1	99.2	42.7	99.8