

## **Branched benzocyclobutene polysiloxane with excellent photo-patterned and low dielectric properties**

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## ■ Experimental

### ● Materials

4-Bromobenzocyclobutene (4-BrBCB,99.8%), Beichuan Tianuo Photoelectric Materials Co. Ltd. Trimethoxy-vinylsilane (> 98%), dimethoxymethyl vinyl silane (> 98%), dimethylvinyl ethoxysilane(>98%) , Palladium acetate (Pd(OAc)<sub>3</sub>, > 98%) and tri-*o*-methylphenylphosphorus (P(*o*-Tol)<sub>3</sub>, > 98%) all purchased from Admas. Tetramethylammonium hydroxide (TMAOH), acetonitrile (MeCN) and triethylamine (TEA) were all purchased from Chengdu Kelon Chemical Co. Ltd. Anhydrous sodium sulfate, Chengdu Kelon Chemical Reagent Factory. Toluene, Chengdu Kelong Chemical Reagent Factory. Cyclopentanone (> 97%), Shanghai Aladdin Biotechnology Co. Ltd. 2, 6-bis -(4-azobenzene methylene) cyclohexanone (> 90.0%), Tixiai (Shanghai) Chemical Industry. 3, 3-carbonyl bis (7-diethylaminocoumarin) (> 98%), Shanghai Myrell Chemical. Acetonitrile and triethylamine were re-distilled, and no other chemicals were further purified.

### ● Measurements

Nuclear magnetic resonance Spectrometer (Bruker Avance-600), Bruker, Switzerland; Infrared Absorption Spectrometer (NICOLET-5700), Nicolet Instruments, USA; Differential scanning calorimeter (TA Q200), TA Corporation, USA; Agilent U9820A Nano Indenter G200, Agilent Technology Co. Ltd. Static Thermo-mechanical Analysis (USA-TA-Q400), TA Corporation, USA; Scanning electron Microscope (ZEISS EVO 18), Carl Zeiss, Germany; Optical Microscope (ISH500), Shanghai Rectangular Optics; Glue leveling machine (EZ4), Jiangsu Leibo Instrument; Precision Impedance Analyzer (HR 4294 LCR), Agilent Technologies Ltd.

### ● Synthesis

#### 1. Monomer preparation

Synthesis of three monomers (BCB-T , BCB-D and BCB-S) has been reported in the research work of the research group <sup>1-2</sup>.The specific synthesis scheme is as follows.

4-BrBCB(0.2 mol), trimethoxy-vinylsilane or dimethoxymethyl vinyl silane or dimethylvinyl ethoxysilane (0.3 mol), TEA(0.24 mol), Pd(OAc)<sub>2</sub> (0.6 mmol), P (*o*-Tol)<sub>3</sub> (2.4 mmol), MeCN(200 mL) were added into 500 mL reaction bottle in anhydrous and anaerobic environment, as shown in

Table S1. The system was heated to about 85°C for 24 h, and the color of the system gradually changed from yellow to brown-black during the reaction process, and acicular crystals were gradually precipitated in the system at the later stage of the reaction. The reaction mixture is quickly pumped and filtered through a silica gel sand core funnel, repeated three times, and the needle-like solid in the funnel is fully washed with petroleum ether. The mixed organic solvent solution was concentrated by vacuum evaporator and then distilled under reduced pressure to obtain light yellow liquid, and three target products were obtained, namely BCB-T, BCB-D and BCB-S (60-70% yield).

## **2. Preparation of branched benzocyclobutene polysiloxane resin**

BCB-T(3mmol), BCB-D (12mmol or 27mmol or 57mmol), TMAOH (0.2wt% (BCB-T+BCB-D)), toluene and ultra-pure water were added to the reaction bottle at 80°C for 10 h, BCB-S (8.2 mmol) diluted with toluene was added, and the temperature was raised to 100°C for 4 h. After water washing, organic phase drying, concentration and petroleum ether removal, the viscous yellowish liquid was obtained. After drying at 100°C in vacuum oven for 24 h, three kinds of branched benzocyclobutene polysiloxane resins with different proportions of HBPSi-1, HBPSi-2 and HBPSi-3 were obtained.

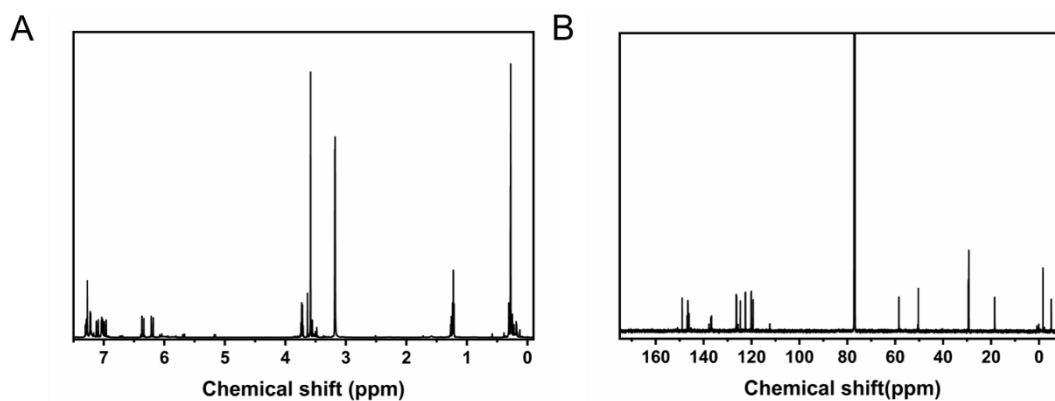
## **3. Preparation of branched resin photosensitive film**

The branched benzocyclobutene polysiloxane resin (1 g), 2, 6-bis -(4-azobenzene methylene) cyclohexanone (BAC) (0.03 g), 3,3' -carbonyl bis (7-diethylaminocoumarin) (0.01 g) were added into a 3mL brown sample bottle, and the solvent toluene: cyclopentanone (mass ratio 3:1) was added. Ultrasound promotes the dissolution of photosensitizer to obtain a photosensitive solution; The photosensitive film was obtained by spinning the photosensitive solution with drying solvent at 80°C A 365nm UV-LED point light source was used to cure the photosensitive film through the mask plate. After the development solution (cyclohexanone: petroleum ether =4:1), the pattern consistent with the mask plate was obtained. At last, the film after photocuring was subjected to a programmed temperature rise process. The temperature rise process was kept in 160°C for 2 h, 180°C for 2 h, 200°C for 2 h, 220°C for 2 h, 240°C for 1 h, and the film with high crosslinked density was obtained by natural cooling.

**Table S1** Material ratio of branched resin

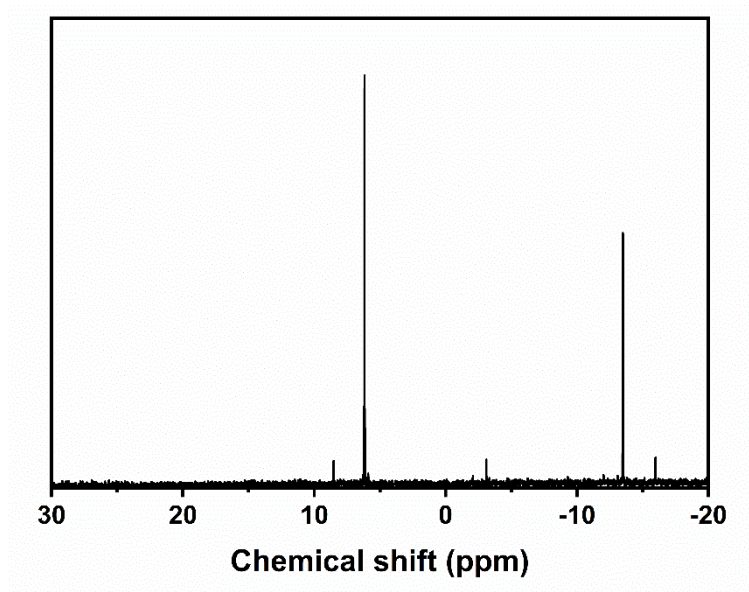
Sample	BCB- T: BCB-D	Si- OCH <sub>3</sub> : H <sub>2</sub> O	BCB-S: Si-OCH <sub>3</sub> (D+T)	TMAOH: (D+T)	Solvent
HBPSi-1	1: 4	1: 5	1: 4	0.2 wt%	toluene
HBPSi-2	1: 9	1: 5	1: 4	0.2 wt%	toluene
HBPSi-3	1: 19	1: 5	1: 4	0.2 wt%	toluene

Note: All ratios are molar ratios



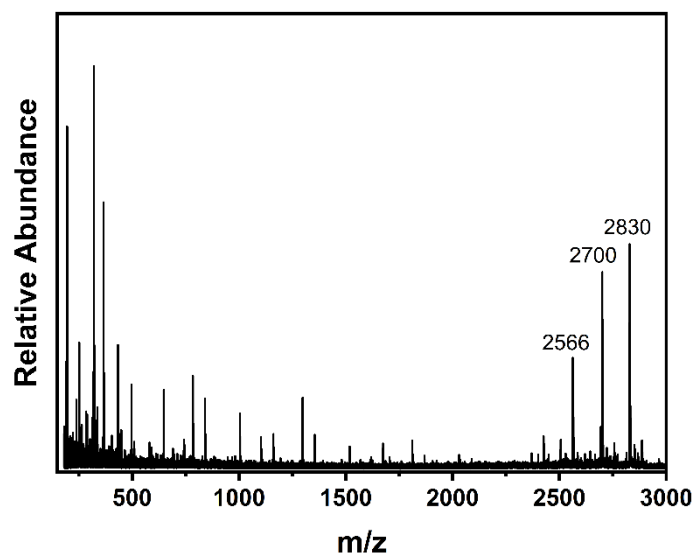
**Fig. S1.** (A) and (B)  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum of **HBPSi-2** resin

It can be seen that 0-0.3 ppm is the chemical shift of H on Si-CH<sub>3</sub> in resin, 3.17 ppm is the chemical shift of H on BCB quaternary ring in polymer, and about 6.3 ppm is the chemical shift of H on vinyl. About 6.8-7.3 ppm is the chemical shift of H in the benzene ring. The chemical shifts of about 1.25 ppm and 3.6 ppm may be H of methyl groups on the incomplete methoxy group and methyl and methylene groups on the ethoxy group. From the  $^{13}\text{C}$  NMR, it can be seen that the chemical shift of the carbon of Si-CH<sub>3</sub> in the polymer resin is about -1.67 ppm, the carbon of the methylene and methyl groups of ethoxysilane in the capping agent is about 18.5 ppm, and 58.46 ppm, respectively, the carbon of the benzocyclobutylene quaternary ring is about 29.26 ppm and 29.5 ppm, the carbon of the vinyl group in the polymer is about 120.18 ppm and 122.53 ppm, and the chemical shift of the carbon of the benzene ring in the polymer is 124.65 ppm, 137.02 ppm, 146.09 ppm, 146.57 ppm, 146.85 ppm, 148.95 ppm. The results showed the successful preparation of branched polysiloxane resin.



**Fig. S2.**  $^{29}\text{Si}$  NMR spectrum of **HBPSi-2**

As shown in Fig.S2 of the  $^{29}\text{Si}$  NMR spectrum, about 6 ppm is the disiloxane structure in the branched polysiloxane resin, and about -14 ppm is the chemical shift of silicon in the trisiloxane structure.



**Fig.S3** Mass spectrometry of **HBPSi-2** resin.

Molecular weight characterization of HBPSi-2 polymer resin by time-of-flight mass spectrometry. As shown in Fig.S3, there are small molecular fragments in the resin, which indicates to a certain extent that the degree of hydrolysis condensation is low, and there are many oligomers in the resin. Higher values at 2566 m/z, 2700 m/z, and 2830 m/z are the main molecular segment fragments of resin-cured cross-linking. The difference may be due to the mass of several alkoxy groups (-OCH<sub>3</sub>, -OCH<sub>2</sub>CH<sub>3</sub>).

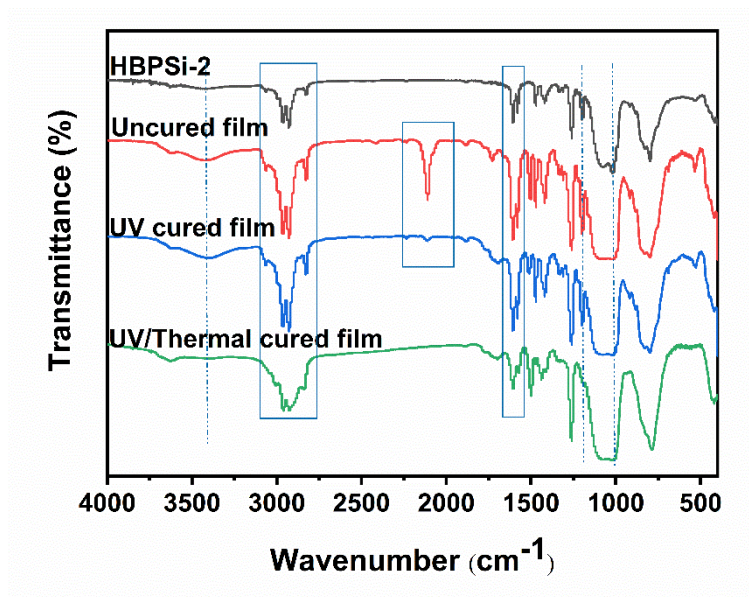


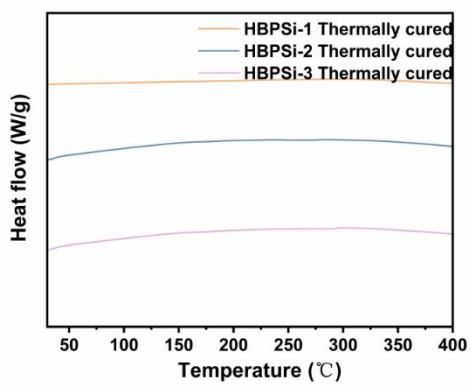
Fig. S4. FT-IR spectrum of different curing states



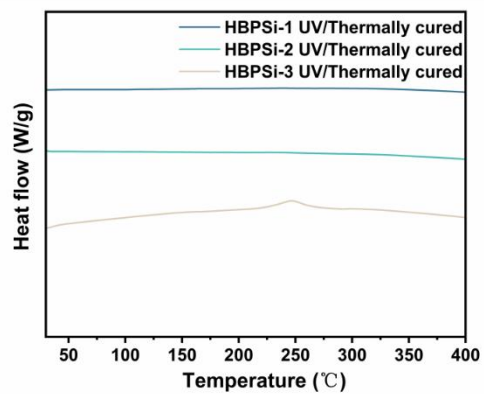
**Table S2** DLS test of **HBPSi-2**

Sample ID	Eff. Diam. (nm)	Polydispersity
HBPSi-2-1	467.43	0.235
HBPSi-2-2	505.30	0.294
HBPSi-2-3	481.60	0.213
Mean:	484.78	0.247
Std Err:	11.05	0.024
Std Dev:	19.13	0.042

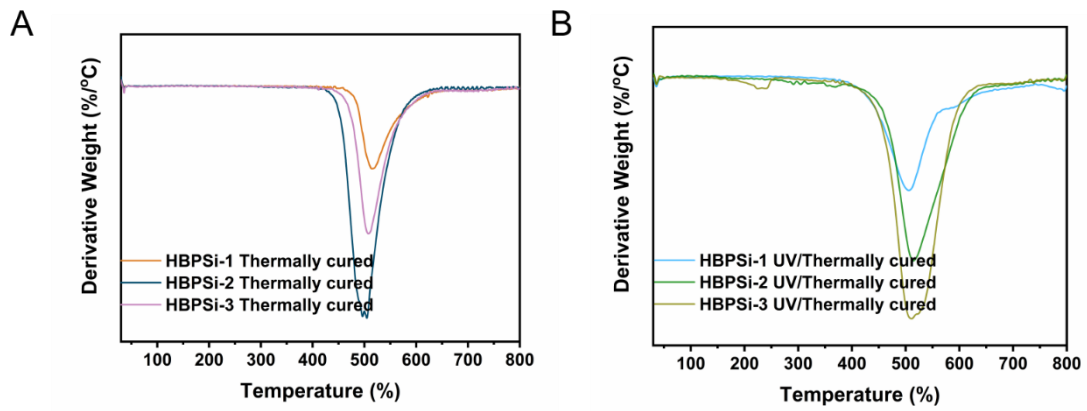
A



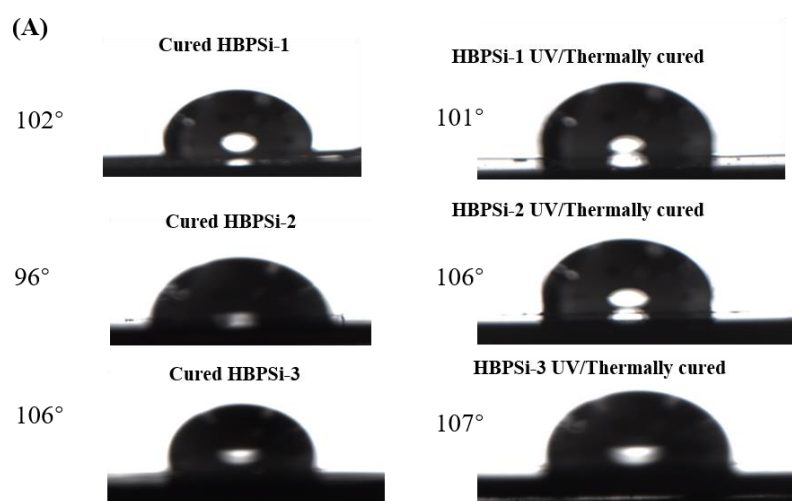
B



**Fig. S5.** (A), (B) DSC spectrum of thermal curing and photothermal curing resin



**Fig. S6.** (A), (B) DTG spectrum of thermal curing and photothermal curing resin



**Fig. S7.** (A) and (B) are the contact angle of the thermocurable and photothermal curable resins

#### Reference

1. Qiu xia Peng, Huan Hu, Yue ting Deng, et al. *Journal of Materials Chemistry C*, 2022, 10, 9106.
2. Qiuxia Peng, Jiajun Ma, Ji Wu, et al. *Polym Chem*, 2023, 14, 3446-3452.