

Electronic Supplementary Information

Flexible and Low-k Polymer Featuring Hard-Soft-Hybrid Strategy

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Experiment Section

1, Materials

Platinum divinyltetramethyldisiloxane (Pt(dvs), 1 wt% in xylene solution) was purchased from Alfa Aesar Company. Phenyltrimethoxysilane, methylchlorosilane and dimethylvinylchlorosilane were purchased from J&K Scientific (China). Hydride-terminated polydimethylsiloxane (PDMS; $M_n = 580$ g/mol) was purchased from Sigma-Aldrich. 3,6-dibromobenzocyclobutene was kindly donated by Beichuan Ruihui Science and Technology Co., Ltd. Tetrahydrofuran (THF) and toluene were dried and freshly distilled under nitrogen (N_2) atmosphere prior to use.

2, Measurements

Fourier transform infrared (FTIR) measurements at $400-4000\text{ cm}^{-1}$ were conducted on a Nicolet FTIR 5700 spectrophotometer at room temperature. The sample films were prepared by casting the solution on KBr plates. ^1H 、 ^{13}C and ^{29}Si NMR spectra were obtained with a Bruker Avance-600 using deuterated chloroform as the solvent and tetramethylsilane as the internal reference. Differential scanning calorimeter (DSC) was conducted under nitrogen at a rate of $10\text{ }^\circ\text{C}/\text{min}$ on a TA instrument 2100. Thermal gravimetric analysis (TGA) was performed on a TA 2100 thermogravimetric analyzer in a nitrogen atmosphere at a rate of $10\text{ }^\circ\text{C}/\text{min}$. UV-Vis spectra of cured PDBD thin films were recorded using a TU1810 spectrophotometer. The molecular weight of PDBDs was determined by gel permeation chromatography (GPC) equipped with refractive index (RI) detector using polystyrene as the standard and THF as the eluent at a flow rate of 1.0 mL min^{-1} . The mechanical properties of cured PDBDs were characterized using an MTS tytron 250 microtensile testing machine. The films had dimensions of approximately $50\text{ mm} \times 20\text{ mm} \times 1\text{ mm}$; the tensile rates were tested at $0.5\text{ mm}/\text{min}$. The dielectric constant and dielectric loss of the resin were measured on an Agilent 4294 A Impedance Analyzer with varying frequencies at ambient temperatures (The $10.0 \pm 0.05\text{ mm}$ diameter cylindrical samples were

polished with thicknesses of 3.0 ± 0.1 mm. After the samples were thoroughly dried under vacuum, gold was deposited via vacuum evaporation on both sides of the samples as electrodes. The final data were obtained from the average of the results in five of the same samples). The dielectric constant was calculated by the following equation:

$$\epsilon_r = (C \times d) / (\epsilon_0 \times S)$$

where C , d and S denote the capacitance, thickness, and electrode area of the materials, respectively. ϵ_0 denotes the permittivity of free space and equals 8.854×10^{-12} F/m.

3. Synthesis of octaphenyldicyclooctasiloxane tetra-sodium silanolate (DDNa)

Phenyltrimethoxysilane (96.0 g, 484 mmol), water (10.0 g, 556 mmol), sodium hydroxide (12.8 g, 320 mmol), and 2-propyl alcohol (300 mL) were added to a 500 mL flask under nitrogen. The mixture was stirred for 24 h with refluxing, and then left at room temperature for 8 h. The precipitate was filtered and washed three times with 2-propyl alcohol, and dried in vacuum at 80 °C for 24 h to obtain a white powder (yield 93.0 %).

4, Synthesis of DDSQ-2H

To a 500 mL flask, the DDNa (11.6 g, 10 mmol), triethylamine (3.0 g, 30 mmol) and THF (300 mL) were added under nitrogen. After methylchlorosilane (2.8 g, 25 mmol) was added slowly, the mixture was stirred at 0 °C for 1 h, then left at room temperature for 6 h. The filtrate was washed with deionized water and saturated NaHCO₃ aqueous solution. The organic layer was dried over magnesium sulfate and concentrated. The solid residue was washed with methanol and acetonitrile, dried in vacuum to give a white solid DDSQ-2H (7.3 g, yield 63.0 %). ¹H NMR: δ 0.14 (d, 6H, -SiCH₃), 4.99 (d, 2H, -SiH), 7.14-7.59 (m, 40H, -PhH). Good correspondence was found in the literature.¹

5, Synthesis of 3,6-bis(dimethylvinylsilyl)benzocyclobutene(DVBCB)

In a 250 mL round-bottom flask, 1,2-dibromoethane (0.1 mL), magnesium (2.64 g,

110 mmol), and dry THF (10 mL) were added. Then 3,6-dibromobenzocyclobutene in (13.2 g, 50 mmol) in THF (50 mL) was added dropwise over a period of 1h and the reaction mixture was heated to 50 °C for another 4 h. After cooled to room temperature, a solution of 13.3 g (110 mmol) of dimethylvinylchlorosilane in 25 mL THF was added into the reaction mixture over a period of 0.5h at ambient temperature. The reaction temperature was elevated to 50 °C and kept overnight. Then the solution was poured into 1 M aq. HCl and extracted with petroleum ether. The organic layer was washed with water and dried over anhydrous sodium sulfate. After removing the solvents, the residual oil was purified by silica-gel column chromatography (petroleum ether) to give the colorless oil (40 mmol, 10.96 g) in 80% yield. ¹H NMR (600 MHz, CDCl₃) δ: 7.36 (s, 2H, ArH), 6.35 (dd, 2H, -CH=CH₂), 6.10 (dd, 2H, -CH=CH₂), 5.81 (dd, 2H, -CH=CH₂), 3.26 (s, 4H, -CH₂-CH₂-), 0.34 (s, 12H, Si-CH₃).

6, Polymer Synthesis

A typical experiment to prepare random copolymer PDBDs is as following: distilled toluene (20 mL), DDSQ-2H, PDMS, DVBCB, and Pt(dvs) (1wt% in xylene, 20 uL) were charged into an anaerobic tube sequentially. The solution was thoroughly deoxygenated by three freeze-pump-thaw cycles and stirred at 80 °C for 24 h. After cooled to room temperature, the solution was poured into a large excess of methanol. The precipitates were dried under vacuum at 80 °C overnight. Three different DDSQ/PDMS ratios were employed to prepare three PDBDs; P1 (The ratio of DDSQ and PDMS groups was 1:4), P2 (The ratio of DDSQ and PDMS groups was 2:3) and P3 (The ratio of DDSQ and PDMS groups was 4:1).

7, Preparation of the cured PDBD resins

The PDBDs were heated at 180 °C for 4 h and then cured stepwise at 200 °C for 4 h, 250 °C for 2 h in a ceramic chip, finally, the PDBDs were converted into an insoluble and infusible resin. The cured films are transparent.

8, Measurement of water uptake

The 10.0 mm diameter cylindrical fully cured samples with thicknesses of 3.0 ± 0.2 mm were dried in a drying oven until constant weight. Then put them into

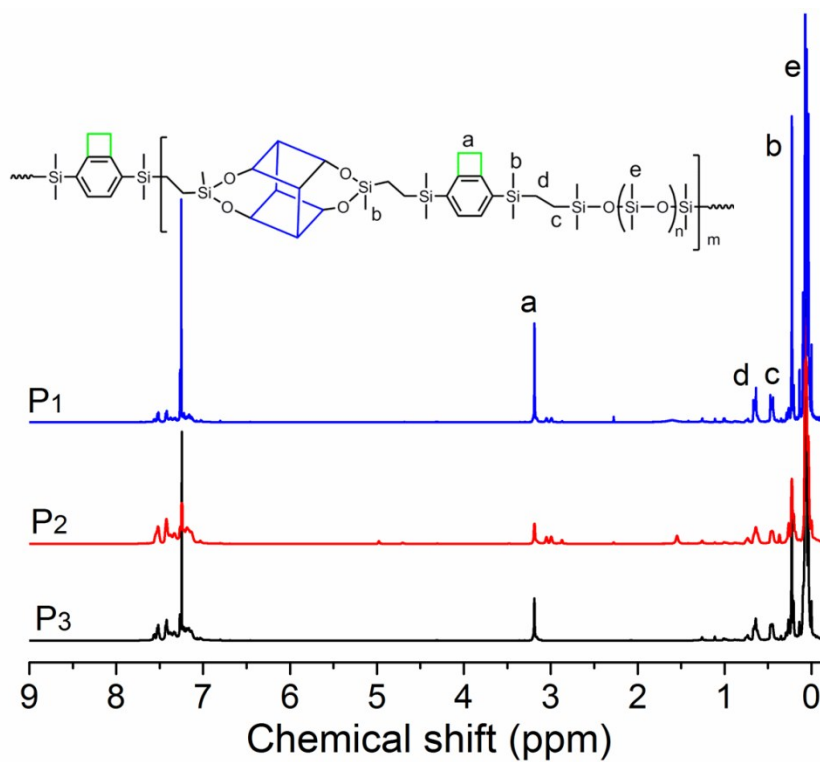


Figure S1. ^1H NMR spectra of PDBD-1, PDBD-2 and PDBD-3.

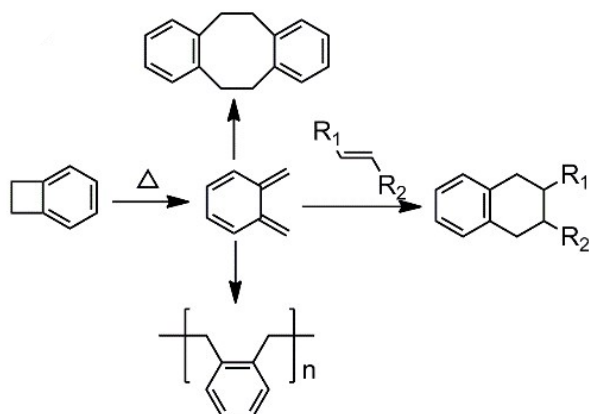


Figure S2. Possible reaction route of BCB group.

Note: the strained four-membered ring of BCB undergoes a ring-opening reaction above 160°C and produces an intermediate, o-quinodimethane. The intermediates react with each other to form 1,2,5,6-dibenzocyclooctadiene dimers, react with dienophiles to form a Diels–Alder adduct, or undergo polymerization.^{2,3}

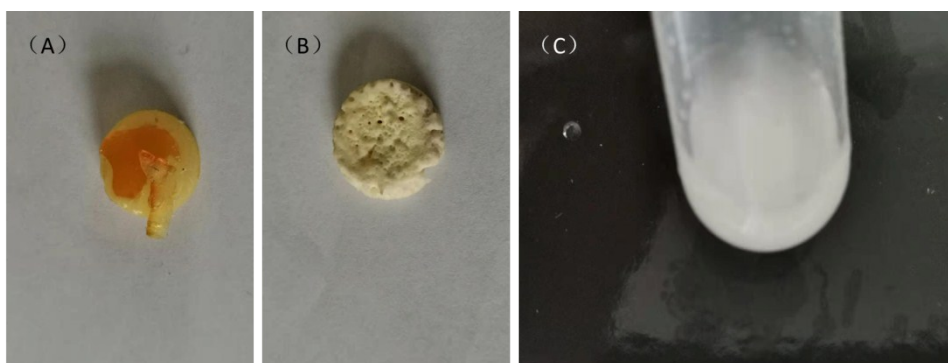


Figure S3. Images of (A) DVBCB and PDMS, (B) DVBCB and DDSQ-2H after thermo-curing at 250 °C for 2 h, (C) DDSQ-2H and PDMS.

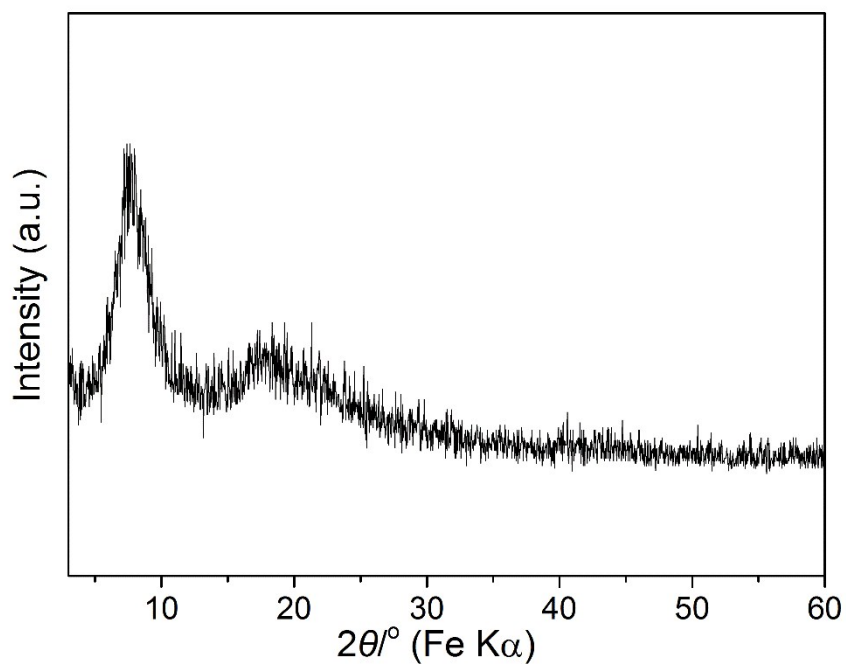


Figure S4. XRD spectrum of the cured PDBD-3 film.

Note: The organic-inorganic copolymers were subjected to wide-angle XRD. For the organic-inorganic copolymers, the XRD curves displayed two broad amorphous peaks at about $2\theta = 7.5$ and 18.4° , respectively, and no sharp diffraction peaks were detected. The results of XRD indicate that the organic-inorganic copolymers were no longer crystalline. It is seen that the diffraction peak at $2\theta = 7.5^\circ$ was detected in the copolymers as in phenyl DDSQ structure.⁴

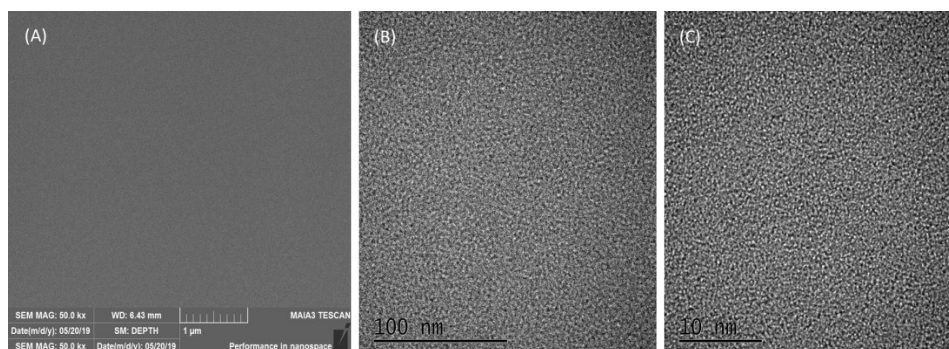


Figure S5. SEM (A) and TEM (B), (C) images of thermally cured PDBD-3 film.

Note: Figure S5 displays SEM and TEM images of thermally cured PDBD-3 film, revealing smooth surfaces and no macrophase separation of the DDSQ and PDMS segments. For comparison, Figure S3 provides images recorded after thermal curing of DVBCB and DDSQ-2H monomer blended with PDMS, but blending PDMS with resulted in macrophase separation. Thus, the combination of the rigid DDSQ cage structure and the flexible PDMS segments in the BCB matrix of PDBD, linked through covalent bonds, improved the thermal and mechanical properties, ensured high transparency and flexibility, and inhibited macrophase separation of the DDSQ cage structures and PDMS segments.

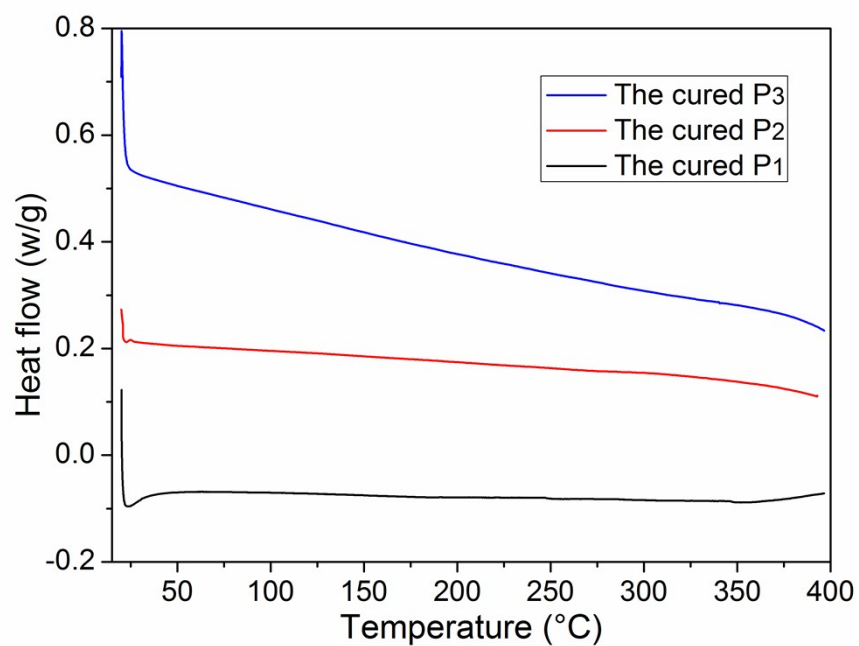


Figure S6. DSC traces of the cured PDBD-1, PDBD-2 and PDBD-3 at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in N_2 .

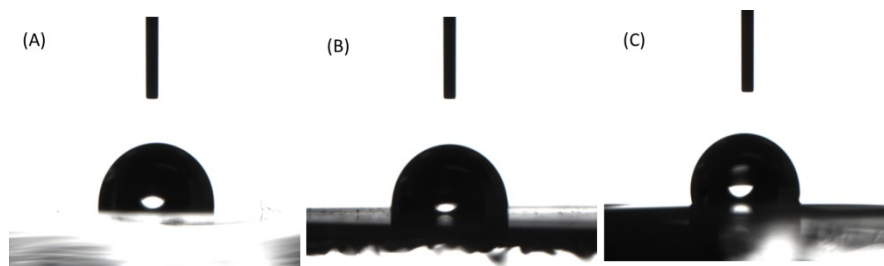


Figure S7. Static contact angle of water on the surface of cured the cured PDBD-1 (A), PDBD-2 (B) and PDBD-3 (C) films (99° , 97° and 101°).

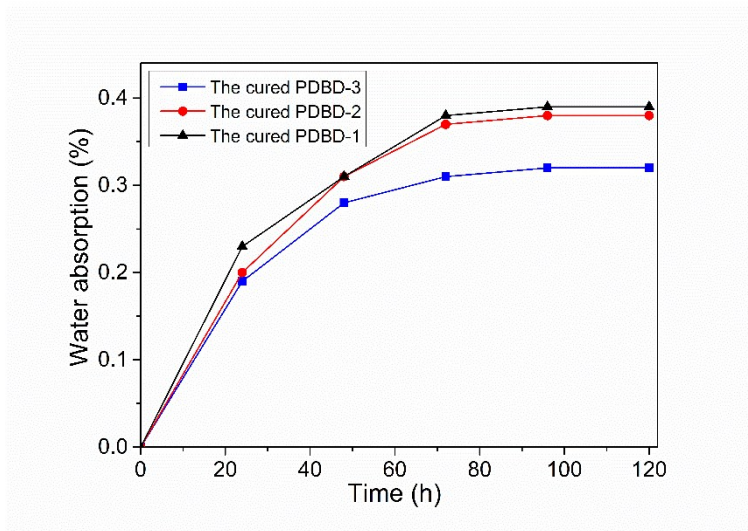


Figure S8. Water uptake of the cured PDBD resins.

Water adsorption is an important parameter for applications of high-performance dielectric materials. We measured the water adsorption of the cross-linked PDBD resins by weighing the changes of the cured samples before and after immersion in boiling water. The water adsorption values of the cured PDBD-1, PDBD-2 and PDBD-3 were 0.39%, 0.38% and 0.32%, slightly higher than other BCB-containing resins, but they also showed good moisture-resistance. To investigate the nature of the low water absorption of the cured PDBD resins, we measured the contact angles of water on the surface of the resulting cured films, and the results were 99° , 97° and 101° . Hence, the cured PDBD films both had a good hydrophobic surface, which offered low water absorption to the hybrid materials. Both the cured PDBD films had hydrophobic surface and low water absorption, which effectively prevented moisture adsorption and deterioration of the dielectric properties, which is important for the application of dielectric materials in the microelectronic and electrical industry.

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