Electronic Supplementary Information

Thermo-curable and	photo	-patternable	polysiloxane	and			
polycarbosiloxane	by	facile	Piers-Rubins	ztajn			
polycondensation and post-modification							
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Synthesis of AB-Fle prepolymers by Piers-Rubinsztajn polycondensation

In the typical synthesis of AB-Fle, 1,1,3,3-tetramethyldisiloxane (5.373 g, 40 mmol), $B(C_6F_5)_3$ (79.8 mg, 0.156 mmol in 2 mL dry o-xylene solution) and dry o-xylene (10 mL) were added to a flame-dried three-neck round-bottom flask under nitrogen. The mixture of dimethoxymethylvinylsilane (3.517 g, 26.6 mmol) and dimethoxydimethylsilane (1.371 g, 11.4 mmol) was diluted with dry o-xylene (10 mL) and added dropwise via a syringe pump over a period of 2.6 h. The polycondensation reaction started after an induction period of approximately three minutes. The start of reaction was indicated by an exotherm and release of a gaseous byproduct. After the addition finished, the reaction mixture was stirred for another 15 minutes to complete the polymerization. Methoxytrimethylsilane (1.5 mL) was added as endcapping reagent. Neutral alumina (approx. 1 g) was added to adsorb the catalyst $B(C_6F_5)_3$ and then filtered. The solvent and excess monomers were removed by rotary evaporation to obtain crude AB-Fle. It was then dissolved in a minimum of toluene and precipitated in methanol. Solvent was decanted from the precipitated polymer, and the residue was dissolved in minimum of toluene again. The above "redissolution and precipitation" steps were repeated further twice. The final residue was concentrated under vacuum to afford a viscous liquid AB-Fle with 33.4% yield.



Fig. S1 Photos of the last precipitation process after P-R polycondensation employed by Ph-bridged hydrosilane (left) and O-bridged hydrosilane (right).



















Fig. S12 29 Si NMR spectra of BCB-Xs in CDCl₃ and their corresponding molecular structures (left).



Fig. S13 APC spectra of BCB-Xs.



Fig. S14 DSC curves at a heating rate of 10 $^\circ\text{C}$ min $^{-1}$ in N_2 atmosphere.



Fig. S15 DMA curves for tan δ at a heating rate of 3 °C min⁻¹ in N₂ atmosphere.



Fig. S17 Molding process of photosensitive and non-photosensitive interlayer dielectric layer.

Synthesis of Photosensitizer



Scheme S1 Synthetic route of photosensitizer.

The photosensitizer was prepared according to the literature¹ partially. Compound **A** (sebacyl chloride, > 95.0%, GC, 1.112 g ,4.65 mmol, TCI) and dichloromethane (5 mL, 99.9%, extra dry with molecular sieves, water \leq 30 ppm, in resealable bottle, Innochem) were added to a round-bottom flask, which was covered by aluminum foil tightly. The mixture was bubbled with nitrogen for 30 minutes at 0 °C to remove oxygen and subsequently stirred for 10 minutes. Compound **B** (4-[3-(trifluoromethyl)-3H-diazirin-3-yl]benzyl alcohol, 2.010 g, 9.3 mmol, 95%, Bidepharm) and dichloromethane (10 mL) were added dropwise via a syringe pump at a rate of 22 mL h⁻¹ to the flask. The reaction was kept stirring at ambient temperature overnight. Solvent was removed under vacuum to obtain light yellowish viscous liquid with a yield of 95.6%. ¹H-NMR (400 MHz, CDCl₃, δ /ppm): 7.39-7.37 (4H, d), 7.20-7.18 (4H, d), 5.11 (4H, s), 2.36-2.32 (4H, t), 1.64-1.60 (4H, m), 1.30-1.27 (8H, m).



Fig. S18 ¹H NMR of photosensitizer in CDCl₃.

Photo-patterning Procedure of BCB-Xs

The reaction solution was prepared with **BCB-X**s (100 mg mL⁻¹) and photosensitizer (10 mg mL⁻¹) in toluene. It was drop-casted onto the surface of a silicon wafer via a spin-coating route (1000 rpm, 10 s; 2000 rpm, 60 s) and baked at 80 °C in vacuum for 5 minutes. The dielectric layer was patterned by exposure under a strip-shaped mask and 365 nm-UV light (using DSX-UVP60 UV LED curing systems) with a dose of about 1000 mJ cm⁻². Postexposure baking was carried out for 2 minutes at 110 °C in air to increase the degree of crosslinking. 2-Butanone was used as a developer to dissolve the unexposed area. The wafer was baked on a hot plate at 250 °C for 1 h to fully crosslink the preserved part. The thickness of the film was around 130 nm. The above experiments were all carried out in the yellow light clean room.

Molar Ratio Effect of Vinyl-containing Dimethoxysilane

Different side groups were introduced into polycarbosiloxanes and polysiloxane to modulate the dielectric and mechanical properties in this work. In order to compare the effects of different side groups, it is necessary to keep the molar ratio of BCB functional groups (i.e. molar ratio of vinyl-containing dimethoxysilane) fixed. Therefore, as shown in **Table S1**, dielectric and thermal properties of cured BCB-functionalized polycarbosiloxane resins have been systematically studied with different BCB molar ratios from 0.1, 0.3, 0.5, 0.7 to 1, respectively. It was found that the lowest dielectric constant (D_k) appeared in the specific ratio of 0.5 (**Sample 3** in **Table S1**), which was consistent with previous reports.² However, low glass transition temperature (T_g) was unfavorable for the practical applications, especially 59.8 °C of **Sample 3** and 1.9 °C of **Sample 2**. As a result, a molar ratio of 0.7 was used in our system.

Table S1 Dielectric properties and thermal stabilities of cured polycarbosiloxane
resins with different molar ratios of BCB groups

Sample	R_1	R_2	x/(x+y)	D_k	tanδ ª	<i>T</i> _g (°C) <i>E</i> ′ ^b (Mpa)		v ^c (10 ³ ·mol·cm ⁻³)	
1	Ph	Ph	0.1	2.53	0.004	-25.2 ^d	-	-	
2	Ph	Ph	0.3	2.68	0.007	1.9 ^d , 15.5 ^e	6.53	0.907	
3	Ph	Ph	0.5	2.42	0.002	59.8 ^e	8.40	1.012	
4	Ph	Ph	0.7	2.61	0.002	>325 ^e	-	-	
5	Ph	Ph	1	2.74	0.001	>325 ^e	-	-	

^a Dielectric loss. ^b Storage modulus at (T_g + 50) ^oC by DMA. ^c Cross-linked density. ^d DSC data. ^e DMA data.

Chemical structure	D_k^a	tanδ	<i>T</i> d₅(°C) ^b	T _g (°C) ^c	E'(GPa) d	k ₁ (k ₂) (%) ^e	literature
	2.69	0.0024	475	257	-	(0.20)	3
	2.47 (at 30 MHz)	0.003	429	-	-	-	4
	2.84	-	437	313	2.1	(0.21)	5
	2.69	-	462	127	1.2	0.6	6
C ₆ H ₁₃ O	2.70	-	437	-	-	-	7
	2.38	0.003	457	-	-	(0.31)	8
	2.50	0.00035	430	353	2.89	-	9
	3.00	0.001	478	113	3.2	-	10
	2.84	0.005	436	-	3.89	-	11
	2.43	0.004	484	>325	1.88	(0.19)	This work

Table S2 Structures and properties of benzocyclobutene functional compounds

^a dielectric constant at room temperature at 1 kHz. ^b TGA data, N₂, 10 °C min⁻¹. ^c DMA data. ^d storage modulus by DMA. ^e water absorption at room temperature (in boiling water).

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