## Supplementary Materials

## Facile Strategy for Intrinsic Low-к Dielectric Polymers: Molecular Design Based on Space Charge Conservation

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Figure S1. (a) FT-IR and (b) <sup>1</sup>H NMR of SBI monomer.



Figure S2. 3D electrostatic potential distribution of the DFDPM, BAF and SBI monomer.



Figure S3. High resolution <sup>1</sup>H NMR of PAEKs.



Figure S4. high-resolution XPS spectra of C1s of PAEKs.



Figure S5. XRD patterns of the PAEKs powders.



Figure S6. (a) Dielectric constant and (b) dielectric loss of commercial PEEK.

Table S1. The proportion of C, O and F in the PAEKs.

PAEKs	C content (%)	O content (%)	F content (%)	
PAEK-BAF	80.37	14.63	5.01	
PAEK-8F2S	80.15	15.39	4.45	
PAEK-6F4S	80.41	15.42	4.18	
PAEK-4F6S	82.98	13.45	3.57	
PAEK-2F8S	84.69	13.27	2.04	
PAEK-SBI	81.2	17.99	0.81	

Table S2. XRD peak angles of all samples and their corresponding interchain spacing.

PAEKs —	Рс	Powders		Annealed sheets		
	20 (°)	Distance (nm)	2θ (°)	Distance (nm)		
PAEK-BAF	16.15	0.5503	16.33	0.5424		
PAEK-8F2S	16.62	0.5348	16.72	0.5298		

PAEK-6F4S	16.80	0.5292	16.85	0.5278
PAEK-4F6S	17.22	0.5163	17.92	0.4946
PAEK-2F8S	17.57	0.5061	17.77	0.4987
PAEK-SBI	17.62	0.5047	17.73	0.4999

**Table S3.** The comparison of dielectric properties of this work with literature reports.<sup>[1-10]</sup>

Polymers	Test frequency	Dielectric properties (room temperature)		Dielectric properties (high temperature)		Ref.	
		κ	Tan δ	κ	Tan δ	Temp.	
PAEK-4F6S	1 MHz	1.98	0.0024	2.05	0.0053	150°C	This work
PAEK-4F6S	9 GHz	1.79	0.0054	-	-	-	This work
Fluoropolymer	30 MHz	2.33	0.0012	-	-	-	[1]
Fluoropolymer	10 GHz	2.89	0.0061	-	-	-	[2]
BCB-based polymer	30 MHz	2.77	0.007	-	-	-	[3]
BCB-based polymer	1 MHz	2.72	0.0055				[4]
EP	1 MHz	3.23	0.018	-	-	-	[5]
POSS-based polymer	1 MHz	2.88	0.01	-	-	-	[6]
LCP	10 GHz	2.9	0.0027	-	-	-	[7]
Poly(aryl ether)	1 MHz	-	-	2.4	0.004	215°C	[8]
PI	10 KHz	2.09	0.0012	-	-	-	[9]
MOF	1 MHz	3.05	-	3.06	-	350K	[10]

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