Supporting Information for:

Oxygen-free Polymers: New Materials with Low Dielectric Constant and Ultra-low Dielectric Loss at High Frequency

Jiaren Hou[a], Jing Sun[a,b,*], and Qiang Fang[a,*]

a. Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China

b. CAS Key Laboratory of Energy Regulation Materials Shanghai Institute of Organic Chemistry, 345 Lingling Road, Shanghai 200032, P. R. China.

***Corresponding authors.**

E-mail: qiangfang@sioc.ac.cn (Q. Fang); sunjing@sioc.ac.cn （J. Sun）

Table of Content

1. NMR Spectra

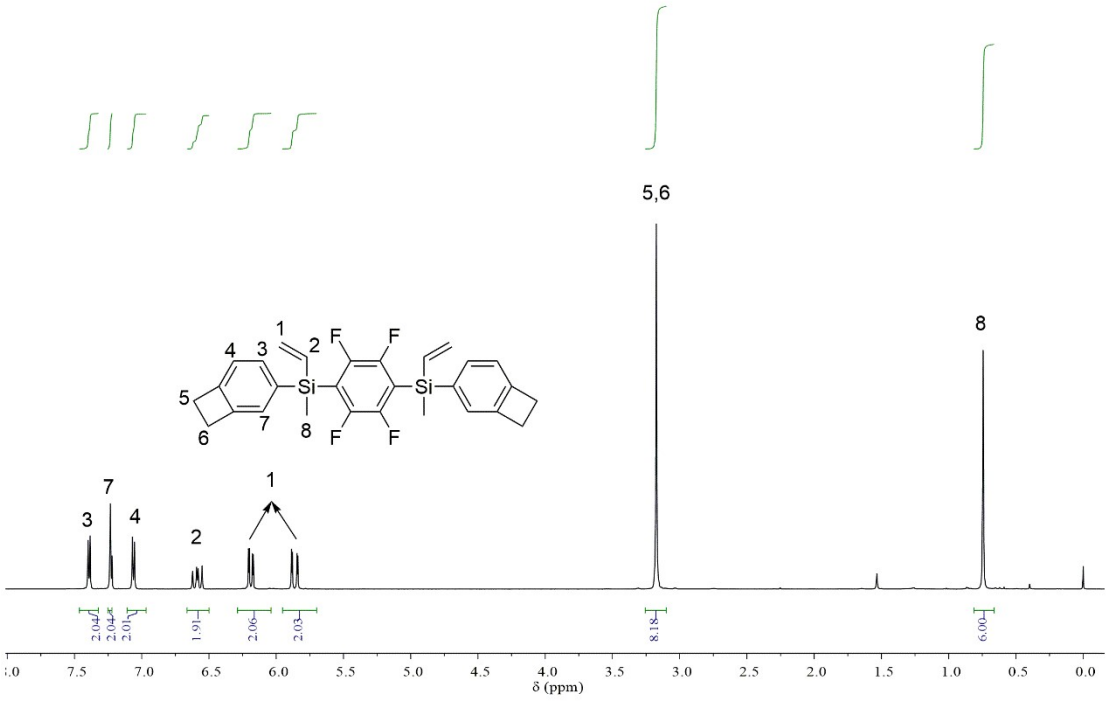


Figure S1. ^{1}H NMR spectrum of 4F-BVS (500 MHz, $CDCl_3$)

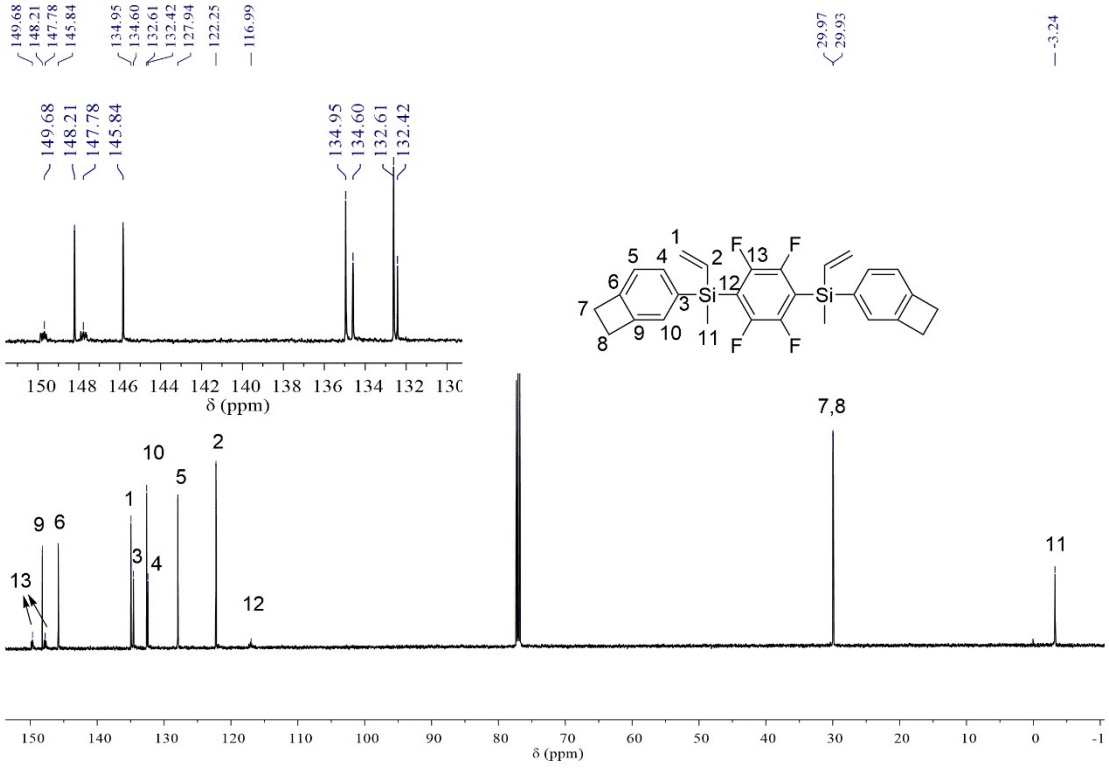


Figure S2. ^{13}C NMR spectrum of 4F-BVS (126 MHz, $CDCl_3$)

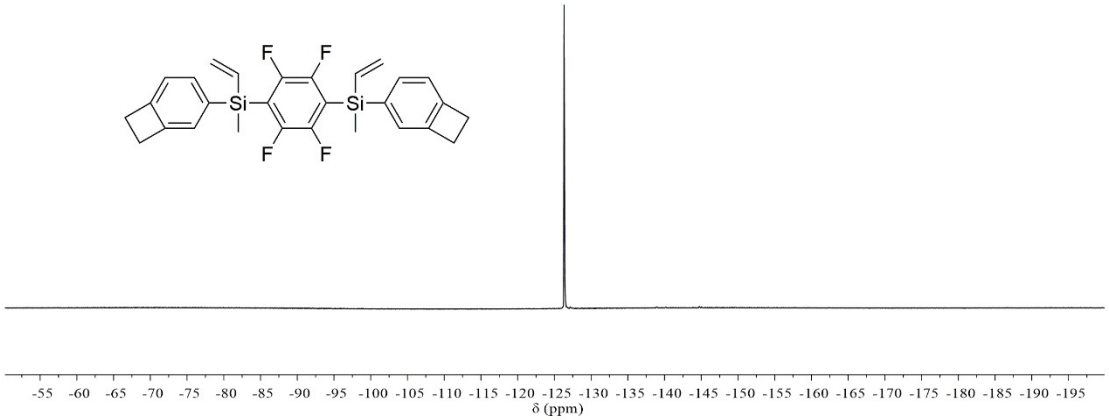


Figure S3. ^{19}F NMR spectrum of 4F-BVS (376 MHz, $CDCl_3$)

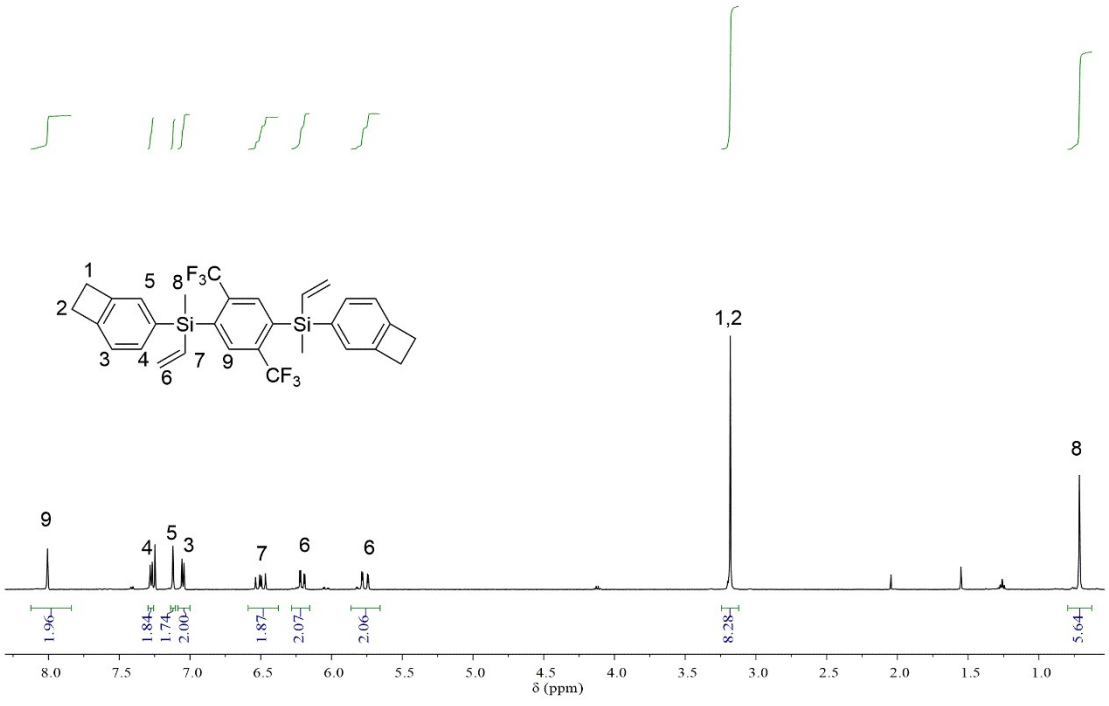


Figure S4. ^{1}H NMR spectrum of 6F-BVS (500 MHz, $CDCl_3$)

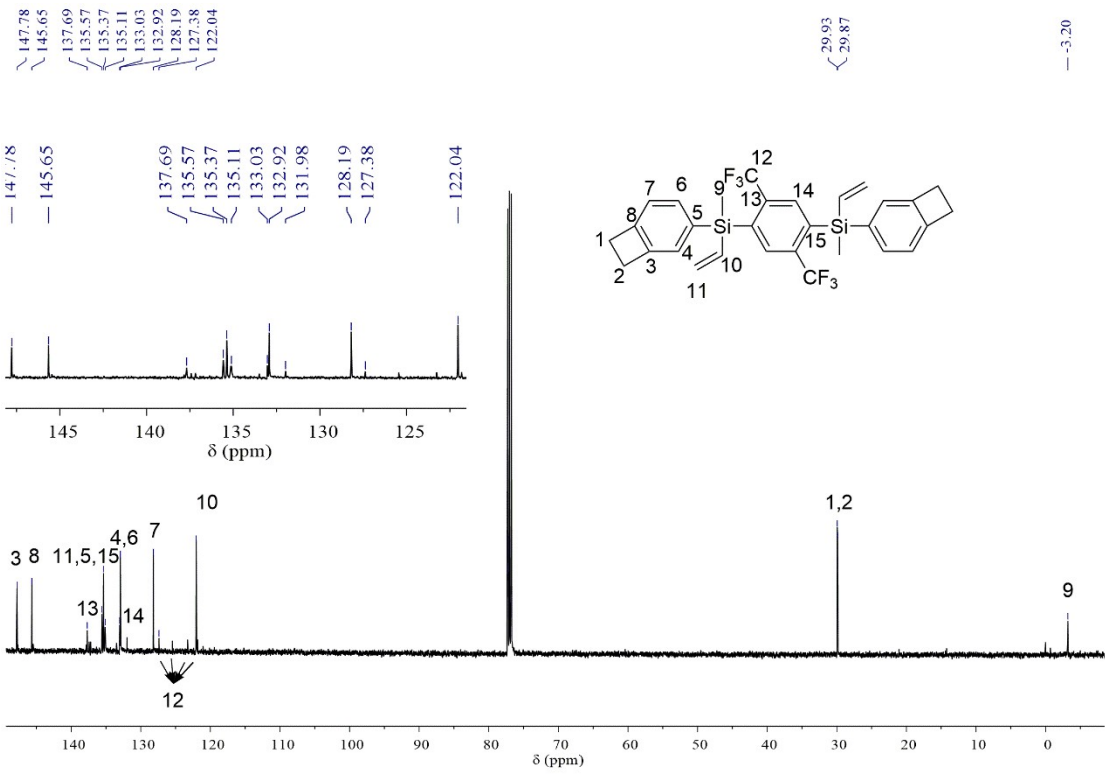


Figure S5. ^{13}C NMR spectrum of 6F-BVS (126 MHz, $CDCl_3$)

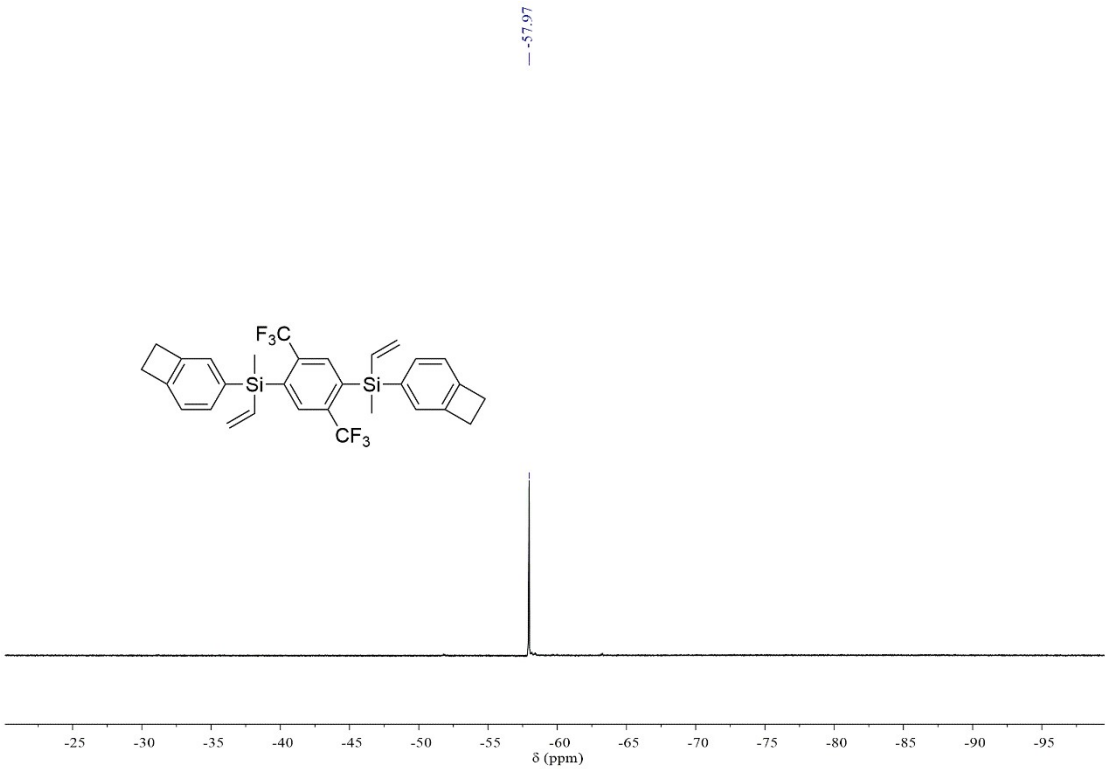


Figure S6. ^{19}F NMR spectrum of 6F-BVS (376 MHz, $CDCl_3$)

2. Determination of Crosslinking Density Parameters

Table S1. The mass of polymer sample before swelling in xylene (m_0), the mass of swelling to equilibrium (m_1), and the mass after drying up to constant weight (m_2).

Resins	m_0/mg	m_1/mg	m_2/mg	Φ^a/%
p-4F-BVS	446.3	446.8	446.2	99.98
p-6F-BVS	450.9	451.3	450.8	99.98
p-6F-BCB	445.5	446.1	445.4	99.98

a: The gel fraction is calculated by Equation: $\Phi = m_2/m_0 \times 100\%$.

3. Determination of Polymer-Solvent Interaction Parameters

The polymer solvent interaction parameters can be calculated by the following equation[1].

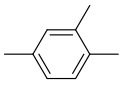
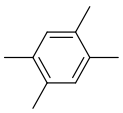
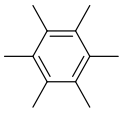
$$\chi = 0.34 + V_s/RT(\delta_p - \delta_s)^2 \qquad \text{Eq. S1}$$

Where V_s is the molar volume of solvent (121.9 cm^3/mol), R is the gas constant (8.314 J/ (mol·K)), and T is the absolute temperature (298.15 K), δ_p and δ_s are the solubility parameters of the polymer and the solvent, respectively. The value of δ_s is 18.4 $J^{1/2}cm^{-3/2}$, and the δ_p can be calculated by the following formula.

$$\delta_p = (E_{coh}/V_p)^{1/2} \qquad \text{Eq. S2}$$

Where E_{coh} is the cohesive energy of the polymer, and V_p is the molar volume of the polymer. The cohesive energy and molar volume could be estimated by the group increment method. The group increments involved are listed in Table S2[2].

Table S2. Group contribution to cohesive energy (E_{coh}) and Van der Waals volume ($V_{w,p}$) according to Fedors.

Group	$E_{coh,i}$ (J/mol)	$V_{p,i}$ (cm^3/mol)	Group	$E_{coh,i}$ (J/mol)	$V_{p,i}$ (cm^3/mol)
$-CH_2-$	4940	16.1		3390	0
$-CH_3$	4710	33.5		31940	33.4
$-CF_3$	8370	46.8		31940	14.4
-O-	3350	3.8		31940	-23.6
-F	4190	18.0			

The interaction parameters according to equations S1 and S2, and the results are shown in Table S3.

Table S3. The calculation of polymer-solvent interaction parameters

polymer	E_{coh} (J/mol)	V_p (cm^3/mol)	δ_p ($J^{1/2}cm^{-3/2}$)	χ
p-4F-BVS	168300	311.0	23.3	1.50
p-6F-BVS	168280	370.6	21.3	0.76
p-6F-BCB	139020	246.8	23.7	1.74

4. References

1. Jain, S. R.; Sekkar, V.; Krishnamurthy, V. N., Mechanical and Swelling Properties of Htpb-Based Copolyurethane Networks. *Journal of Applied Polymer Science* **1993,** *48*, 1515-1523.
2. Krevelen, D. W. V., *Properties of Polymers*. Elsevier: New York, 1997; p 196-197.