Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Understanding How Intrinsic Micro-pores Affect the Dielectric Properties of Polymers: An Approach to Ultra-low Dielectric Polymers with Bulky Tetrahedral Units as Cores

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This supplemental document contains 6 figures and two equations over 6 pages.

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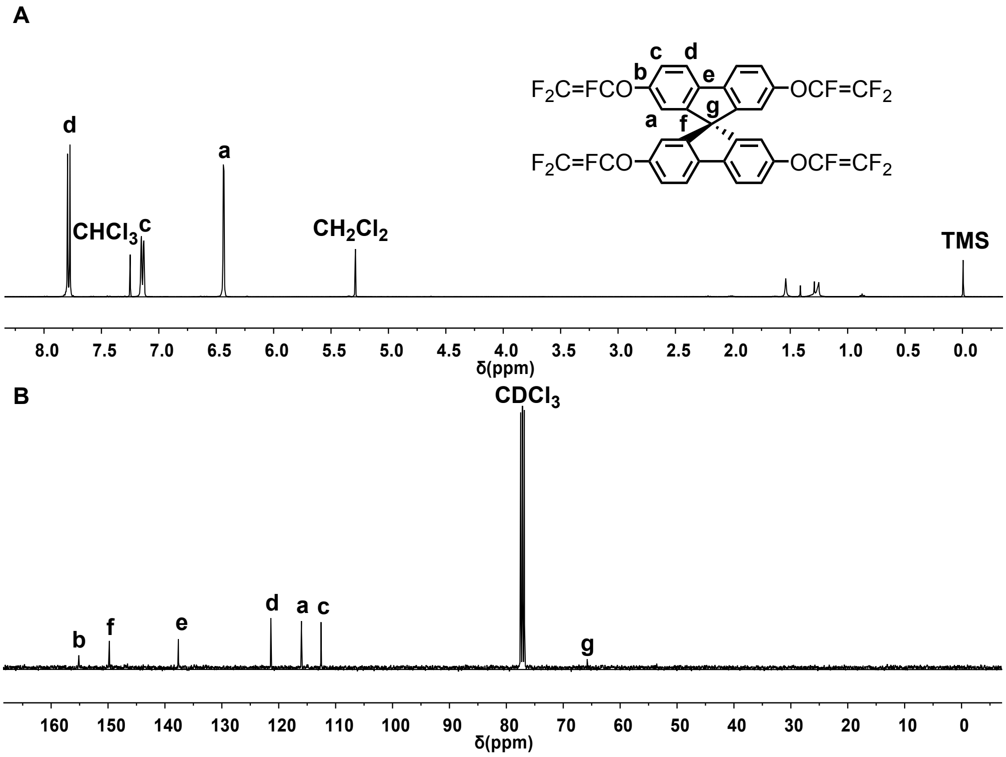

Fig. S1 ^{1}H NMR spectrum (up, 400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (down, 100 MHz, $CDCl_3$) of **4a**.

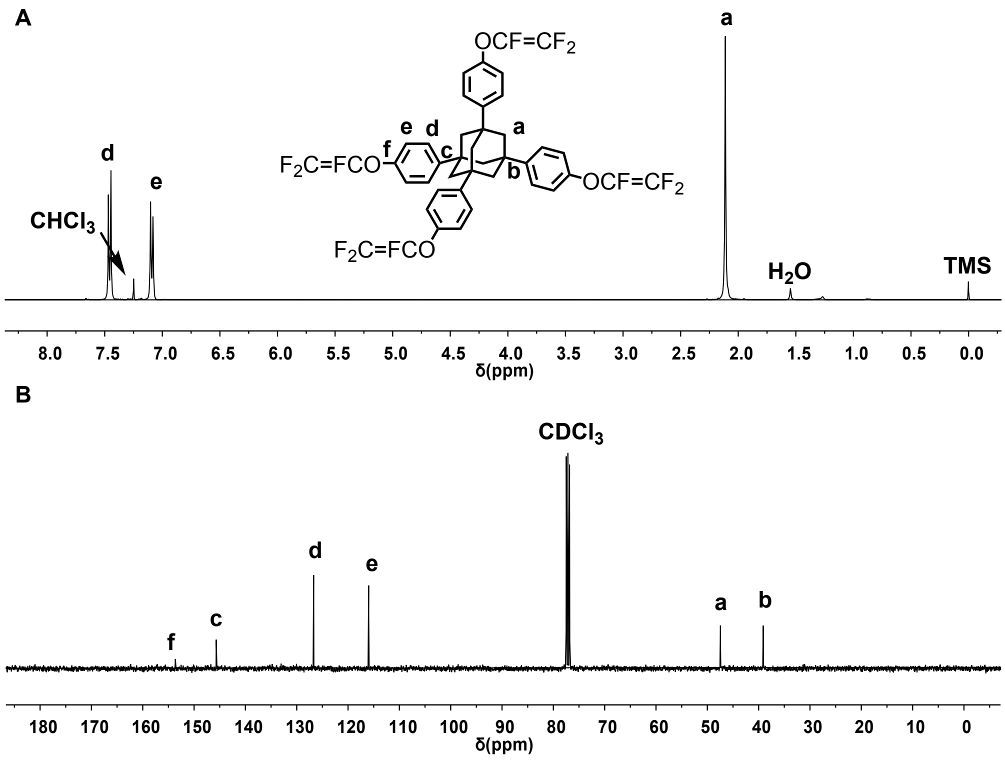

Fig. S2 ^{1}H NMR spectrum (up, 400 MHz, $CDCl_3$) and ^{13}C NMR spectrum (down, 100 MHz, $CDCl_3$) of **4b**.

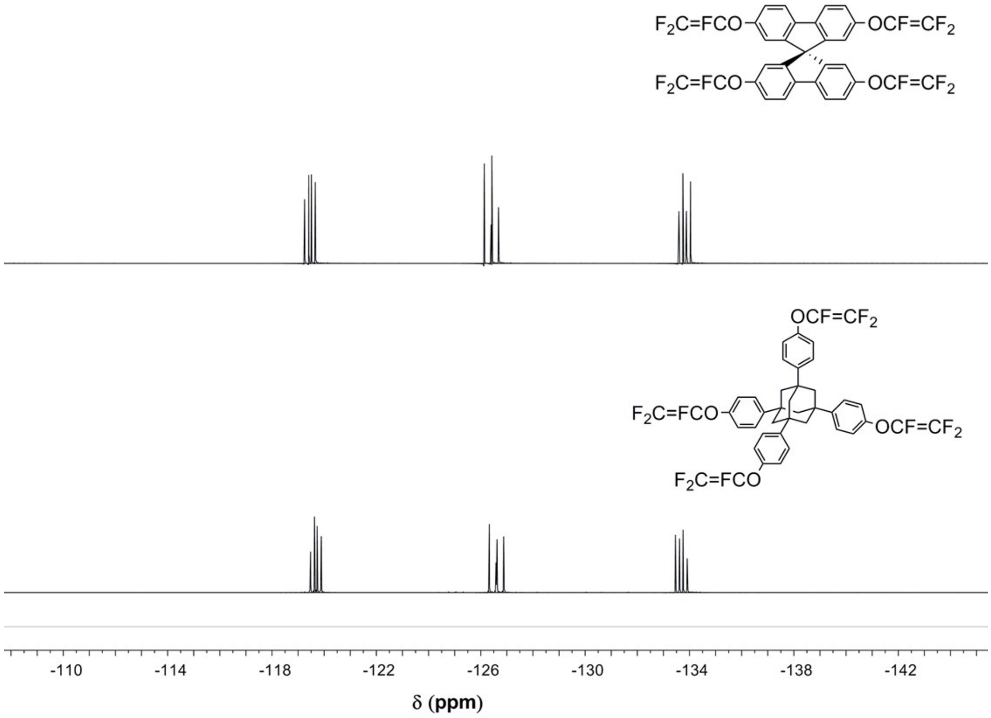

Fig. S3 ^{19}F NMR spectra (376 MHz, $CDCl_3$) of monomers **4a** and **4b**.

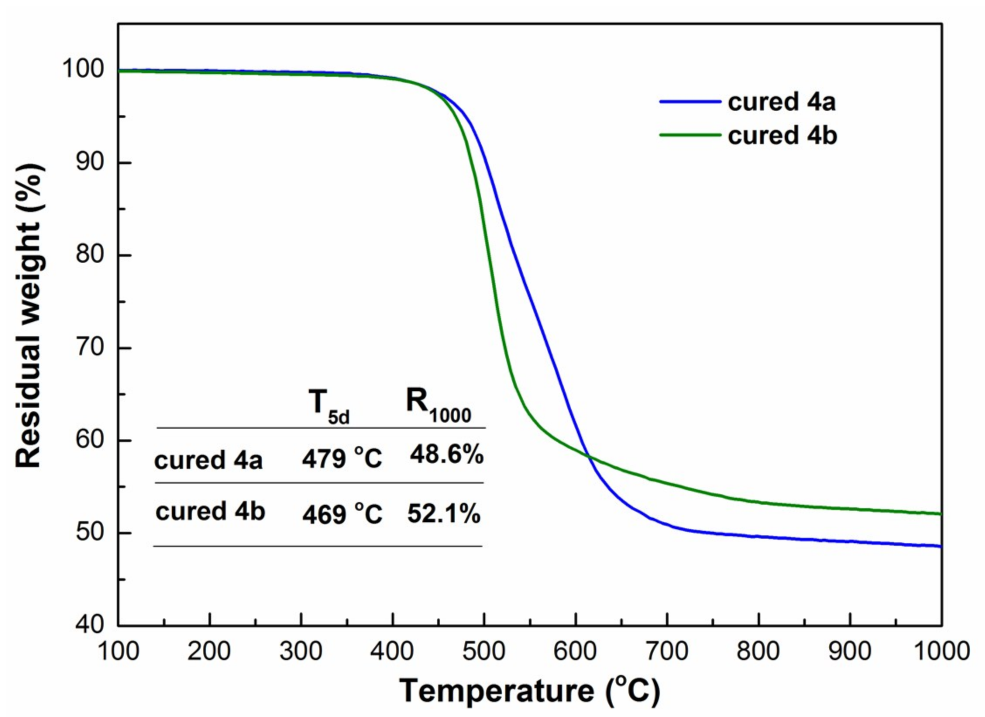

Fig. S4 TGA curves of **4a** and **4b** in N_2 with a heating rate of 10 ^{o}C min^{-1}.

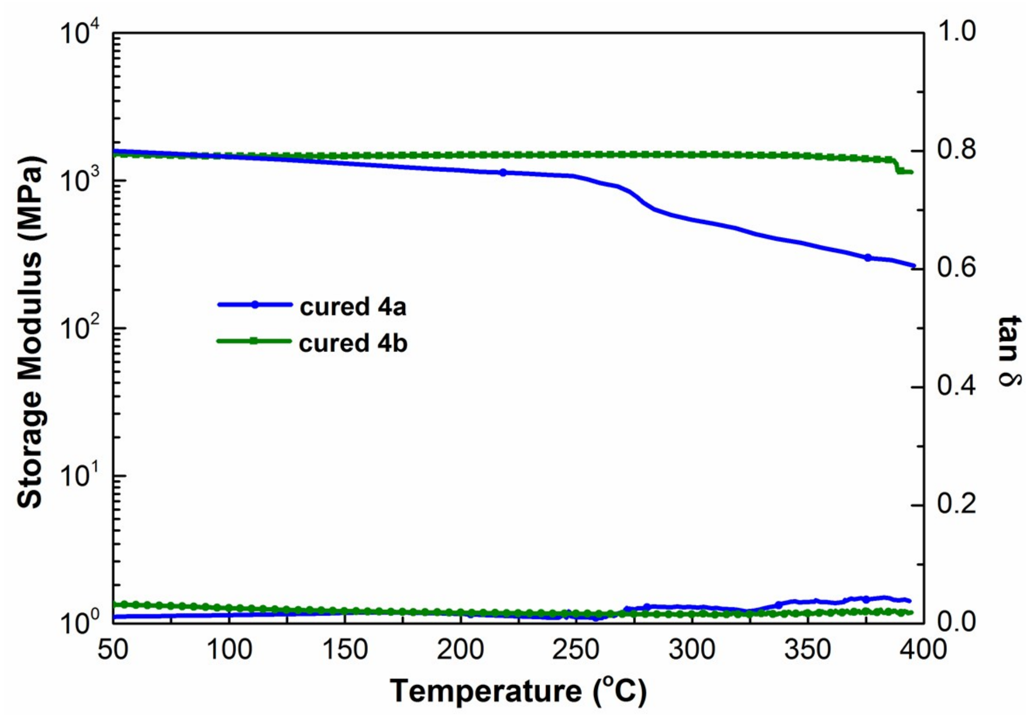

Fig. S5 DMA curves of cured **4a** and cured **4b** at a heating rate of 5 °C min^{-1} in air.

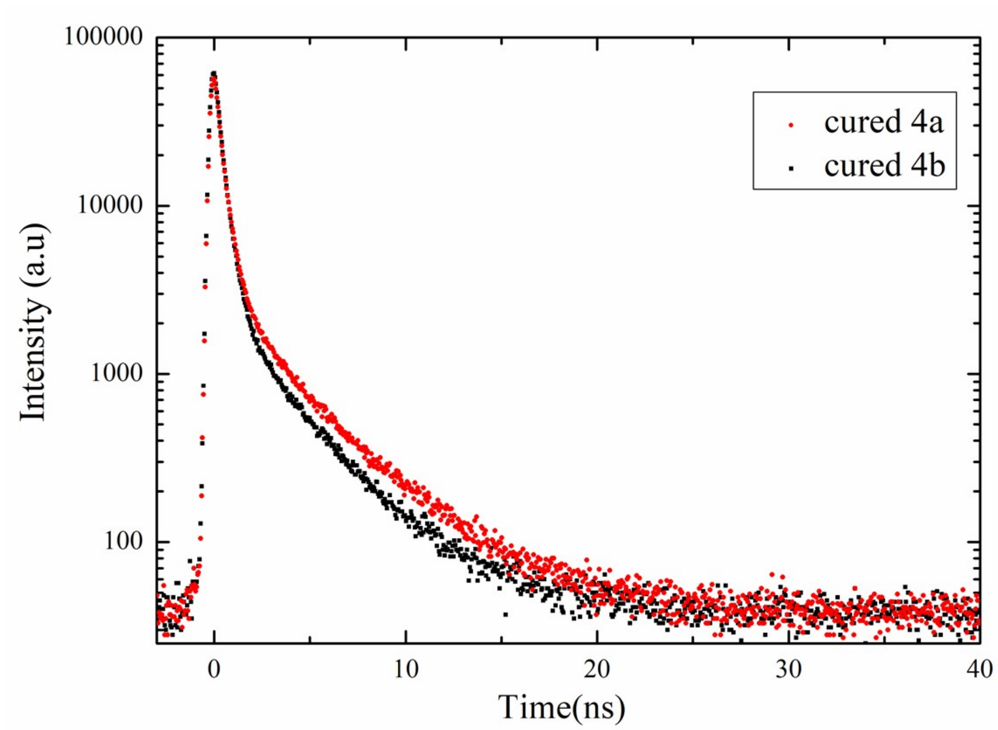

Fig. S6 Positron lifetime distribution spectra measured for cured **4a** and cured **4b**.

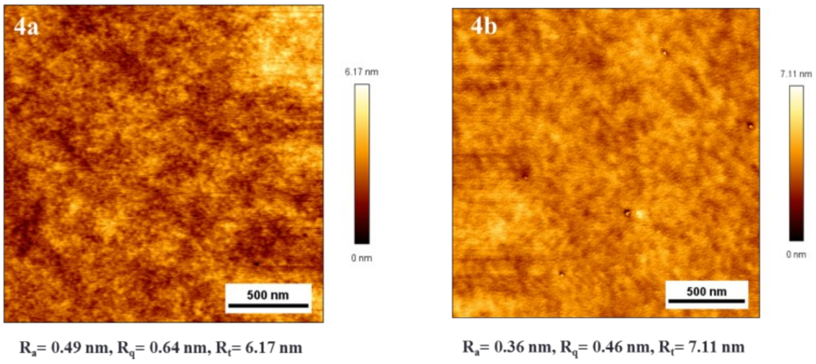

Fig. S7 AFM images of cured **4a** and cured **4b** films on silicon wafers.

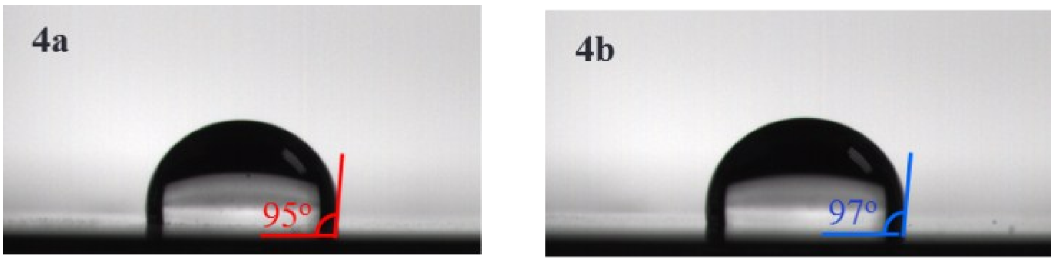

Fig. S8 Pictures of the contact angle of water of cured **4a** and cured **4b** films on silicon wafers.

Equation 1 and 2.

$$\tau_3 = \frac{1}{2}[1 - \frac{r}{r+\Delta r} + \frac{1}{2\pi}\sin\left(2\pi\frac{r}{r+\Delta r}\right)]^{-1} \quad \text{(Eq. S1)}$$

$$f_V = CV_f I_3 \quad \text{(Eq. S2)}$$

where τ_3 (ns) is the o-Ps lifetime, r (Å) represents the average radius of a free volume pores, which is assumed to be spherical, and Δr is the fitted empirical electron layer thickness (1.66 Å). f_V is the fraction free volume, V_f (= $4\pi r^3/3$, in $Å^3$) is the volume of free volume holes and C is empirically determined to be 0.0018 from epoxy data and the WLF (Williams-Landel-Ferry) free-volume equation.

The route for the measurement of dielectric constant using non-contact parallel-plate capacitor method.

The preparation of the samples. A cylindric test sample with average diameters of 15.0 mm was polished until the thickness of the sample was uniform before test.

Calibration of the instrument. Agilent 4294A Precision Impedance Analyzer equipped with the 16451B electrodes (Guarded electrode and Unguarded electrode) should be calibrated three times with a Teflon standard sample sheet until a constant value of 2.1 was achieved.

The measurement. A non-contact mode means that the Guard electrode does not touch the test material in the process of testing. In addition to instrument calibration, following two steps completes the testing process.

Step 1 Place test material between the two electrodes. Then adjust the electrode spacing and make the distance between the Guard electrode and the test material is less than 10% of the thickness of test material. Get capacitance C_{s2} and dissipation D_2 are obtained from Agilent 4294A.

Step 2 Remove tested material and get capacitance C_{s1} and dissipation D_1, which is actually the capacitance and dissipation of a certain thickness of air.

D_k and D_f of test material were obtained automatically by Equation S3 and Equation S4:

$$D_k = \frac{1}{1 - (1 - \frac{C_{s1}}{C_{s2}}) \times \frac{t_g}{t_a}} \qquad \text{(Eq. S3)}$$

$$D_f = D_2 + D_k \times (D_2 - D_1) \times \left(\frac{t_g}{t_a} - 1\right) \qquad \text{(Eq. S4)}$$

Where,

C_{s1} Capacitance **without** test material inserted;

D_1 Dissipation factor **without** test material inserted;

t_g Gap between Guarded electrode and Unguarded electrode;

C_{s2} Capacitance **with** test material inserted;

D_2 Dissipation factor **with** test material inserted;

t_a Average thickness of test material;

D_k Dielectric constant of test material;

D_f Dielectric factor of test material.

Table S1 Crystal data for compound **4b**

Identification code	mo_d8v18538_0m

Empirical formula	C42 H28 F12 O4	
Formula weight	824.64	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I -4	
Unit cell dimensions	a = 17.3865(8) Å	□= 90°.
	b = 17.3865(8) Å	□= 90°.
	c = 7.1447(4) Å	□ = 90°.
Volume	2159.8(2) $Å^3$	
Z	2	
Density (calculated)	1.268 Mg/m^3	
Absorption coefficient	0.116 mm^{-1}	
F(000)	840	
Crystal size	0.180 x 0.110 x 0.070 mm^3	
Theta range for data collection	1.656 to 24.989°.	
Index ranges	-20<=h<=20, -18<=k<=20, -8<=l<=8	
Reflections collected	5508	
Independent reflections	1890 [R(int) = 0.0337]	
Completeness to theta = 25.242°	96.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6111	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1890 / 177 / 187	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0670, wR2 = 0.1883	
R indices (all data)	R1 = 0.0744, wR2 = 0.1995	
Absolute structure parameter	-0.2(6)	
Largest diff. peak and hole	0.435 and -0.184 e.$Å^{-3}$	