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 ¹H NMR spectrum (up, 400 MHz, CDCl₃) and ¹³C NMR spectrum (down, 100 MHz, CDCl₃) 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.

![NMR Spectra](image)

**Fig. S3** $^{19}$F NMR spectra (376 MHz, CDCl$_3$) of monomers 4a and 4b.

![F NMR Spectra](image)

**Fig. S4** TGA curves of 4a and 4b in N$_2$ with a heating rate of 10 °C min$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>$T_{5d}$</th>
<th>$R_{1000}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cured 4a</td>
<td>479 °C</td>
<td>48.6%</td>
</tr>
<tr>
<td>cured 4b</td>
<td>469 °C</td>
<td>52.1%</td>
</tr>
</tbody>
</table>

![TGA Curves](image)
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.

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

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

where \( \tau_3 \) (ns) is the o-Ps lifetime, \( r \) (Å) represents the average radius of a free volume pores, which is assumed to be spherical, and \( \Delta r \) is the fitted empirical electron layer thickness (1.66 Å). \( f_V \) is the fraction free volume, \( V_f (= 4\pi r^3 / 3, \text{in Å}^3) \) 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:

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

$$D_f = D_2 + D_k \times \left( D_2 - D_1 \right) \times \left( \frac{t_g}{t_a} - 1 \right)$$  \hspace{1cm} (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  
\[ a = 17.3865(8) \text{ Å} \quad \square = 90^\circ. \]
\[ b = 17.3865(8) \text{ Å} \quad \square = 90^\circ. \]
\[ c = 7.1447(4) \text{ Å} \quad \square = 90^\circ. \]
Volume  2159.8(2) Å³
Z  2
Density (calculated)  1.268 Mg/m³
Absorption coefficient  0.116 mm⁻¹
F(000)  840
Crystal size  0.180 x 0.110 x 0.070 mm³
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 F²
Data / restraints / parameters  1890 / 177 / 187
Goodness-of-fit on F²  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