Observation of Tunable Refractive Indices and Strong Intermolecular Interactions in Newly Synthesized Methylene-Biphenylene-Bridged Silsesquioxane Thin Films

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**Supporting Figure S1.** Solid state $^{29}$Si-NMR spectra of the methylene-biphenylene-bridged silsesquioxane thin films. The overlapped peaks for the 0 and 100 mol% MBP were deconvoluted assuming Gaussian/Lorentzian peaks.

**Supporting Table S1.** Summary of areas for $T_1$, $T_2$, and $T_3$ and calculated degree of condensation for the 0 and 100 mol% MBP thin films, based on the results of the solid state $^{29}$Si-NMR.

<table>
<thead>
<tr>
<th></th>
<th>area $T_1$</th>
<th>area $T_2$</th>
<th>area $T_3$</th>
<th>deg. of condensation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBP 0 mol%</td>
<td>0</td>
<td>7.8</td>
<td>92.2</td>
<td>97.4</td>
</tr>
<tr>
<td>MBP 100 mol%</td>
<td>1.4</td>
<td>34.9</td>
<td>63.7</td>
<td>87.5</td>
</tr>
</tbody>
</table>

**Solid state $^{29}$Si-NMR measurements.** Solid state $^{29}$Si-NMR has been developed as a powerful technique for investigating the microstructure of silicone-containing materials and hence, employed under the following conditions: Cross polarization (CP) and magic angle spinning (MAS) on a Bruker Avance 400 spectrometer at a frequency of 79.54 MHz with a contact time of 5 ms and a spinning rate of 7 kHz; $^{29}$Si chemical shifts were referenced to a 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) standard (0 ppm).
Solid State $^{29}$Si-NMR Results. Prior to discussion, the following information requires introduction: silsesquioxanes with one siloxane bond are denoted as $T^1$ - RSi(OR)$_2$(O$_{1/2}$)$_1$; those with two siloxane bonds, $T^2$ - RSi(OR)$_1$(O$_{1/2}$)$_2$; those with three siloxane bonds, $T^3$ - RSi(O$_{1/2}$)$_3$.$^{1,2}$

As shown in Fig. S1, the 0 mol% MBP thin film shows two peaks at -59.1 and -68.1 ppm, which can be assigned to the $T^2$ and $T^3$ species, respectively.$^{2,3}$ The 100 mol% MBP thin film shows three peaks at -51.7, -62.4, and -73.8 ppm, which can be assigned to $T^1$, $T^2$, and $T^3$ species, respectively.$^{1,4,5}$ Both the 0 and 100 mol% MBP thin films show the peaks of the $T^1$ and/or $T^2$ species, indicating the presence of Si-OH groups, which are also detected by FT-IR in the range of 940 - 960 cm$^{-1}$ in Fig. 1.$^6$ Regardless, in the case of 0 mol% MBP, the $T^2$ species was detected by $^{29}$Si-NMR and the Si-OH groups were undetected by the FT-IR as the amount of the Si-OH groups in the 0 mol% MBP thin film may have been insufficient for detection by FT-IR.

In addition, the $^{29}$Si CP MAS NMR may be used for evaluating the degree of condensation (DC) by examining the contribution of various silicon species present in the condensed materials.$^1$ In order to obtain accurate DC values, differences in the rate of magnetization transfer to the different sites must be corrected for because the CP rates are dependent on the distance to and the number of hydrogen atoms in the solid
and because the system is typically not allowed to fully relax or reach thermodynamic equilibrium.\footnote{1} Nevertheless, DC values, without the correction, have been simply calculated by the following equation:\footnote{4}

\[ DC = \frac{0.33I(T^1) + 0.67I(T^2) + I(T^3)}{\sum I(T^n)} \]

where $I(T^n)$ represents the area under each $T^n$ peak ($n = 0 - 3$). The overlapped peaks were deconvoluted assuming Gaussian/Lorentzian peaks in order to measure the relative areas of the $T^n$ peaks, as shown in Fig. S1. As summarized in Table S1, the calculated DC values are 97.4 and 87.5% for the 0 and 100 mol% MBP thin films, respectively, indicating that the 0 mol% MBP thin film is more condensed than the 100 mol% MBP thin film.

Moreover, establishment of a correlation between the results of the solid state $^{29}$Si-NMR and that of the FT-IR in terms of Si-O-Si bond angles has been attempted. It proved nearly impossible to clearly explain the bond angles with the $^{29}$Si-NMR results as the chemical shifts were closely related to not only the Si-O-Si bond angles, but also electron density. Indeed, the peaks of the 25, 50, and 75 mol% MBP thin films in the $^{29}$Si-NMR are overlapped in a complex manner. Thus, there were too many possibilities to account for, resulting in huge arbitrariness, even though researchers have investigated
and later revealed the inverse relationship between chemical shifts in $^{29}$Si-NMR and the Si-O-Si bond angles in both experimental and theoretical points of view.$^{7-9}$

References


Complete Author List of Reference 1


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