Homogeneously and gradually anchored self-assembled monolayer by tunable vapor phase-assisted silanization

Grégoire Souharce, Jannick Duchet-Rumeau, Daniel Portinha,* and Aurélia Charlot*

Université de Lyon, F-69631, Lyon; INSA Lyon, F-69621, UMR CNRS 5223, Ingénierie des Matériaux Polymères F-69621, Villeurbanne, France. Fax: +33 (0)4 72 43 85 27; Tel: +33 (0)4 72 43 63 38; E-mail: daniel.portinha@insa-lyon.fr, aurelia.charlot@insa-lyon.fr

Electronic Supporting Information

Determination of the Surface Energies

The surface energies of ODMS monolayers were estimated as a function of exposure time. We used the Fowkes-van Oss-Chaudhury-Good model. It describes the total surface energy as a combination of dispersive interactions (Lifshitz-van der Waals) and polar interactions (Lewis acid-base).

\[ \gamma_{\text{total}} = \gamma_{\text{LW}} + \gamma_{\text{AB}} \]

where \( \gamma_{\text{LW}} \) is the dispersive (or Lifshitz - van der Waals) component. Chaudhury demonstrated that the dispersion (London), induction (Debye) and dipole (Keesom)
contributions to the apolar component are additive. $\gamma^{AB}$ refer to the polar (or Lewis acid-base) components and is given by

$$\gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-}$$

where the electron donor parameter is designated as $\gamma^-$ (basic component) and the electron acceptor one is designated as $\gamma^+$ (acidic component). Then, using the Dupré equation gives

$$\gamma_L (1 + \cos \theta) = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+})$$

Three independent equations are obtained by measuring the contact angle of three liquids (2 polar and 1 dispersive) for which the parameters $\gamma_L^+, \gamma_L^-$ and $\gamma_L^{LW}$ are known.

<table>
<thead>
<tr>
<th>Liquids</th>
<th>$\gamma^{-\text{total}}$ (mJ/m$^2$)</th>
<th>$\gamma_L^{LW}$ (mJ/m$^2$)</th>
<th>$\gamma_L^{AB}$ (mJ/m$^2$)</th>
<th>$\gamma_L^+$ (mJ/m$^2$)</th>
<th>$\gamma_L^-$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Glycerol</td>
<td>64.0</td>
<td>34.0</td>
<td>30.0</td>
<td>3.92</td>
<td>57.4</td>
</tr>
<tr>
<td>$\alpha$-bromonaphtalene</td>
<td>44.4</td>
<td>44.4</td>
<td>$\approx0$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 1. (a) Total surface energy as a function of the exposure time (grafting of ODMS at 60 °C) and (b) magnification for time comprised between 2 and 60 min. The reported errors refer to the standard deviation for each independent experiment.
Figure 2. AFM phase images of ODMS-grafted silicon obtained after grafting time of 4 min, 40 min and 60 min (pictures (A), (B) and (C) respectively).
Figure 3. Intensity of C1s (A) and F1s (B) atomic concentration collected on 11 different locations of a silicon wafer firstly exposed to ODMS vapour for 10 min at 110 °C and then exposed to HFDNC vapor for 30 min at 25 °C.
Figure 4. ToF-SIMS positive ion mass spectra of three different locations of a silica surface gradually grafted with ODMS (10 min, 110 °C) and subsequently backfilled with APTES (15 min, 25 °C, ethanol solution).