Supporting Information

Direct Surface Modification of Poly(VDF-co-TrFE) Films by Surface-initiated ATRP without Pretreatment

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1. XPS depth profiling of poly(VDF-co-TrFE)-g-poly(tBA) film using C$_{60}$ sputtering.

Figure S1. Sputter depth profiling of C$_{1s}$, O$_{1s}$ and F$_{1s}$ of poly(VDF-co-TrFE)-g-poly(tBA) by C$_{60}^+$ sputtering. Atomic concentration of C, O, and F were normalized. The sputter rate was 83.3 nm/min.

XPS spectra were recorded on a PHI Quantera SXM (ULVAC-PHI, Chigasaki, Japan) system using a micro-focused (100 μm, 24.8 W, 15kV) Al X-ray beam (1486.6 eV) with a photoelectron take-off angle of 45°. A dual-beam charge neutralizer (10 V - 7 μA for Ar⁺, and 1.0 V - 20 μA for electron beam) was used to compensate the charge-up effect. The C$_{60}^+$ ion source was operated at acceleration voltage of 10 kV with raster area of 2 mm × 2 mm. Analysis size on the sample was φ 0.1 mm. The base pressure of the main chamber (7.0 × 10⁻⁷ Pa) was achieved by evacuation using turbomolecular and ion-getter pumps. The reference specimen for sputter rate measurement was poly(tBA) spin-coated film on Si wafer, of which thickness was determined by ellipsometer. The sputter rate by C$_{60}^+$ ion was determined to be
83.3 nm/min.

As shown in Figure S1, atomic concentration of oxygen gradually decreased and that of fluorine increased with sputtering time. The depth profiles of $O_{1s}$ and $F_{1s}$ indicated that the interface of poly(tBA) and poly(VDF-co-TrFE) was not sharp. Although the outermost surface was almost covered by poly(tBA), there was a mixture region of poly(tBA) and poly(VDF-co-TrFE) inside the film. If we determine the interface between poly(tBA) and poly(VDF-co-TrFE) to be the position when the normalized intensity of $O_{1s}$ was 0.50, it took 0.32 min to achieve the interface by exposure to $C_{60}^+$ beam. The thickness of surface-grafted poly(tBA) layer was estimated by sputter time and sputter rate to be $0.32 \text{ (min)} \times 83.3 \text{ (nm/min)} = 26.6 \text{ (nm)}$.

2. XPS spectra of $C_{1s}$ region of poly(VDF-co-TrFE) and poly(VDF-co-TrFE)-g-poly(tBA) films

![XPS spectra](image)

Figure S2. Narrow scan XPS spectra of $C_{1s}$ region of (a) poly(VDF-co-TrFE) and (b) poly(VDF-co-TrFE)-g-poly(tBA) films
XPS measurement was carried out using an XPS-APEX (Physical Electronics Inc.) at \(1 \times 10^{-9}\) Pa using a monochromatic Al \(K_\alpha\) X-ray source operated at 200 W. XPS spectra were collected at takeoff angle of 45°. High-resolution spectra of the C\(_{1s}\) were acquired at an energy step of 0.1 eV. Peak area ratio of C-F, C=O, C–O, and C–C bonds in Figure S2(b) was estimated by four Gaussian fitting curves, as represented in Table S1.

<table>
<thead>
<tr>
<th>Binding energy, eV</th>
<th>C-F</th>
<th>C=O</th>
<th>C-O</th>
<th>C-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area ratio (obs.), %</td>
<td>3.2</td>
<td>12.4</td>
<td>23.9</td>
<td>60.5</td>
</tr>
<tr>
<td>Area ratio (theo.)(^a), %</td>
<td>0.0</td>
<td>11.1</td>
<td>22.2</td>
<td>66.7</td>
</tr>
</tbody>
</table>

\(^a\) Theoretical ratio of poly(tBA).