

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(*t*BA) film using C₆₀ sputtering.

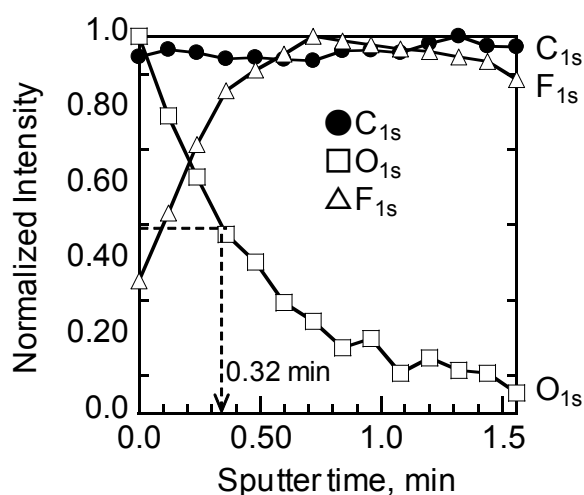


Figure S1. Sputter depth profiling of C_{1s}, O_{1s} and F_{1s} of poly(VDF-*co*-TrFE)-*g*-poly(*t*BA) by C₆₀⁺ sputtering. Atomic concentration of C, O, and F were normalized. The sputter rate was 83.3 nm/min.

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 C₆₀⁺ 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(*t*BA) spin-coated film on Si wafer, of which thickness was determined by ellipsometer. The sputter rate by C₆₀⁺ 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

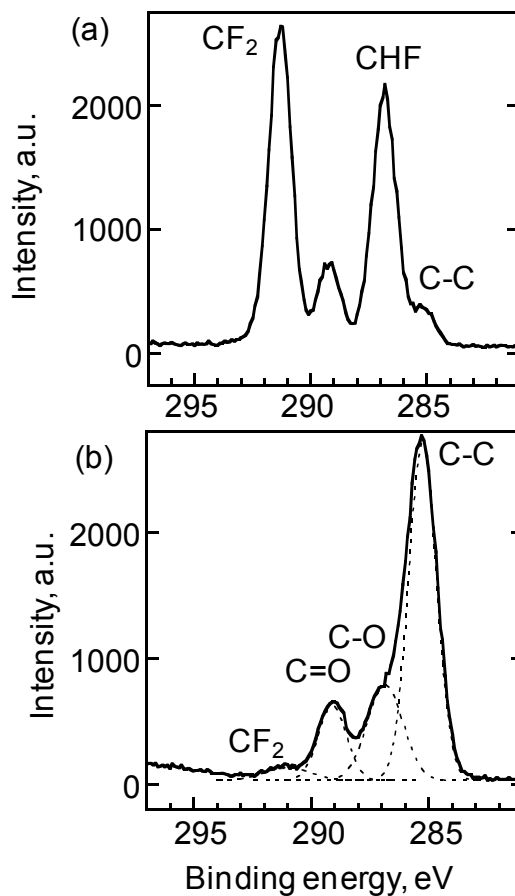


Figure S2. Narrow scan XPS spectra of C_{1s} region of (a) poly(VDF-co-TrFE) and (b) poly(VDF-co-TrFE)-g-poly(tBA) films

XPS measurement was carried out using an XPS-APEX (Physical Electronics Inc.) at 1×10^{-9} Pa using a monochromatic Al K_{α} 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 S1. Area ratio of C-F, C=O, C-O, and C-C bonds of Figure S2(b)

	C-F	C=O	C-O	C-C
Binding energy, eV	291.0	289.09	286.8	285.3
Area ratio (obs.), %	3.2	12.4	23.9	60.5
Area ratio (theo.) ^a , %	0.0	11.1	22.2	66.7

^a Theoretical ratio of poly(*t*BA).