Preparation of Poly(vinylidene fluoride-*co*-trifluoroethylene) Film with a Hydrophilic Surface by Direct Surface-initiated Atom Transfer Radical Polymerization without Pretreatment

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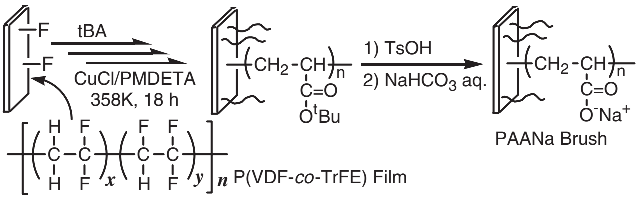
Surface-initiated atom transfer radical polymerization (ATRP) of *tert*-butyl acrylate was carried out directly from a nonmodified poly(vinylidene fluoride-*co*-trifluoroethylene) [P(VDF-*co*-TrFE)] film surface to give a polymer brush, which was further converted to a poly(acrylic acid sodium salt) brush by hydrolysis. A hydrophilic surface was successfully created at the outermost surface of P(VDF-*co*-TrFE) film without any change in the bulk physical properties. Also the effect of surface nanotexture formation on wettability was investigated.

In general, surface roughness enhances water repellency and wettability, which can be explained by two well-known hypotheses proposed by Wenzel and Cassie–Baxter.[1,2] In the Wenzel state, liquid completely wets the grooves or spaces of the rough surface. The area of contact between the solid surface and the liquid increases with surface roughness, resulting in enhancement of the water repellency or wettability. In other words, the apparent contact angle increases for hydrophobic surfaces but decreases for hydrophilic surfaces. In the case of the Cassie–Baxter state, the liquid drop sits on top of the peaks of the rough surface to form air pockets along its contact with the substrate. The surface roughness always increases the apparent contact angle due to the imprisoned air, regardless of the original wettability of the substrate. Although these two theoretical models have been often employed and well studied experimentally by using nanofabricated silicon or inorganic substrates with fabricated pillars or bumps, the wetting behavior of rough surfaces is not fully understood, especially in the hydrophilic region, the transition region between Wenzel and Cassie–Baxter states,[3–5] and on the surface of soft materials such as polymer. We propose here a wettability control method combined with surface-initiated polymerization and nanotexturing in order to investigate the influence of the surface structure on soft materials.

Mayes et al. reported the direct graft copolymerization of methacrylate monomer from a poly(vinylidene fluoride) (PVDF) backbone using atom transfer radical polymerization (ATRP) in a homogenous solution,[6] and suggested that the C–F bond at the secondary halogenated site of PVDF afforded radicals to initiate polymerization, although the crucial evidence to support this hypothesis has not been obtained yet. Chen and his co-workers also prepared a hydrophilic polymer brush on PVDF film by surface-initiated ATRP to control the antifouling properties against protein adsorption.[7] In this work, surface-initiated ATRP was applied to commercially available poly(vinylidene fluoride-*co*-trifluoroethylene) [P(VDF-*co*-TrFE)] film for surface wettability control.

Scheme 1 illustrates the procedure for modifying the film surface. Surface-initiated ATRP of *tert*-butyl acrylate (tBA) was directly conducted from nonmodified P(VDF-*co*-TrFE) film using a CuCl/pentamethyldiethylenetriamine catalyst in the presence of ethyl 2-chloropropionate as a free initiator at 358 K for 18 h. A poly(tBA) (PtBA) brush and unbound polymer are simultaneously produced from the film and free initiator. During the reaction, the film kept the initial size ($12 \times 12\,\mathrm{mm}^2$) without bulk swelling. The reaction temperature was lower than the melting point of P(VDF-*co*-TrFE) (410 K). After the reaction, the resulting P(VDF-*co*-TrFE) film was carefully washed with methanol in a Soxhlet apparatus for 24 h to remove the adsorbed free polymer completely from the surface.



Scheme 1. Surface-initiated ATRP of tBA directly from P(VDF-*co*-TrFE) film to produce polymer brush.

The resulting film surface was analyzed by attenuated total reflection FTIR (ATR-FTIR) using a ZnSe ATR prism. All the spectra are shown in the Supporting Information.[8] The characteristic absorption bands after the ATRP reaction appeared at $1724\,\mathrm{cm}^{-1}$ corresponding to the ester carbonyl group of PtBA. Absorption peaks at 2980 and $3008\,\mathrm{cm}^{-1}$ attributable to the stretching of the C–H bond considerably increased compared with the pristine P(VDF-*co*-TrFE) film. XPS spectra of the PtBA-grafted film exhibited a large decrease in fluorine peak intensity, and an increase in oxygen and carbon peaks. The narrow scan spectrum of $\mathrm{C_{1s}}$ in Figure 1 showed peaks corresponding to the carbons in C=O, C–O, and C–C bonds, respectively. The area ratio calculated by three fitting curves agreed with PtBA. The intensity of $\mathrm{C_{1s}}$ peak due to the C–F bond was very low, indicating that the PtBA brush layer is thick enough to cover the P(VDF-*co*-TrFE) film surface. Although it is not easy to accurately estimate the thickness of the brush layer, $\mathrm{C_{60}}$ sputter XPS measurement suggested that brush thickness is ca. 50 nm.

PtBA grafted onto a P(VDF-*co*-TrFE) film surface was hydrolyzed by immersion in a heptane/water (15/0.1, mL/mL) mixture containing *p*-toluenesulfonic acid monohydrate (1.05 mmol) at 358 K for 6 h. After the reaction, the resulting film was immersed into an aqueous $\mathrm{NaHCO_3}$ solution (1.0 wt %) at 313 K for 1 h, rinsed with a large excess of water, and dried under vacuum for 6 h at room temperature. The transformation of grafting PtBA to poly(acrylic acid sodium salt) (PAANa) by hydrolysis was confirmed by ATR-FT IR and XPS measurements.

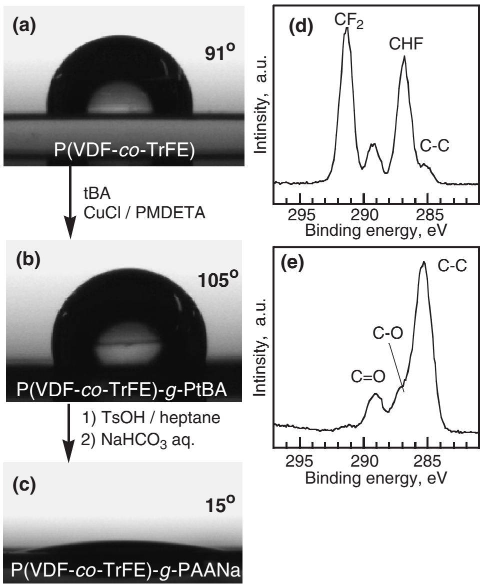


Figure 1. Water droplet shape and XPS C_{1s} spectra of the surface of initial nonmodified (a) and (d), PtBA-grafted (b) and (e), and PAANa-grafted P(VDF-*co*-TrFE) films (c); Water volume = 2.0 μL.

Table 1. Water contact angles on polymer-grafted P(VDF-*co*-TrFE) film surface[a]

	Graft polymer		
	Non	PtBA	PAANa
Before nanoimprint	91°	105°	15°
After nanoimprint	109°	121°	10°

[a]Water volume = 2.0 μL.

The hydrolysis of a grafted polymer can also be followed by water contact angle measurement. As shown in Figure 1 and Table 1, the water contact angle increased from 91 to 105° by surface grafting of PtBA, then decreased to 15° by acidic hydrolysis and neutralization. The surface energy of PAANa-grafted P(VDF-*co*-TrFE) was estimated to be 71 mN/m by the Owens equation. This excellent hydrophilicity of PAANa-grafted polymer film has been maintained for more than 3 months. This is the first successful preparation of a fluoropolymer with stable high surface energy.

The nanotexture of anodic aluminum oxide (AAO) disk was transferred onto a P(VDF-*co*-TrFE) film by nanoimprint technique.[9,10] A P(VDF-*co*-TrFE) film and a commercially available AAO membrane filter with an average pore diameter of 200 nm (Whatman) were sandwiched between a flat silicon wafer on a heating stage,[11,12] and were pressed by a Nanoimprinter NM0401 (MEISYO KIKO Co., Ltd.) at 373 K for 10 min under 30 MPa normal pressure. Then, the film was cooled at room temperature, and the AAO mold was removed. Figure 2 represents the AFM image of the AAO-imprinted surface of a P(VDF-*co*-TrFE) film having many rod-like pillars with ca. 300 nm of diameter. Owing to the tip convolution effect on the AFM image, the apparent pillar diameter is larger than the actual size. Surface-initiated ATRP was carried out directly from the imprinted P(VDF-*co*-TrFE) film to form PtBA brushes on the outermost surface. Subsequent hydrolysis of PtBA gave a poly(acrylic acid) brush. As shown in Figure 2, the original bumpy structure remained even after the surface-initiated polymerization, although the gap between pillars was apparently reduced owing to the formation of grafted layer on the pillars.

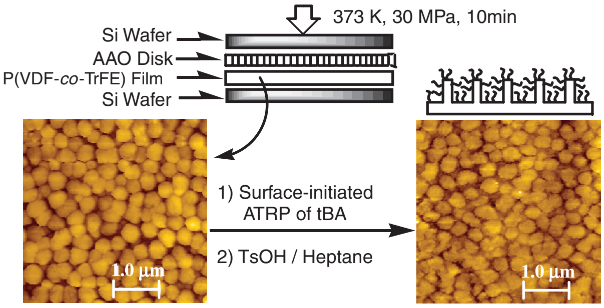


Figure 2. AFM images of the imprinted P(VDF-*co*-TrFE) surface (left) using an AAO membrane filter as a mold, and the corresponding surface after surface-initiated polymerization of tBA and hydrolysis (right).

The water contact angle of P(VDF-*co*-TrFE) surface increased from 91 to 109° by the nanotexture formation due to the existence of an air layer between the water droplet and valley between the pillars. The surface nanotexture also enhanced the water repellency of the PtBA-grafted surface. On the other hand, the contact angle of the PAANa-grafted imprint surface was 10°, which was slightly lower than that of flat surface. This result could be explained by the Wenzel-type wetting or hemiwicking effect due to the hydrophilic pore. As far as we know, there is no other fluoropolymer with such high wettability.

In conclusion, we proposed a method to control the surface wettability of fluoropolymer film through a combination of direct surface-initiated ATRP and surface nanotexture formation.

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