Macromolecules **1996,** *29,* 4155−4157

Communications to the Editor

Excimer Laser-Induced Surface Reaction of Fluoropolymers with Liquid Water

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Received November 14, 1994
Revised Manuscript Received March 19, 1996

Surface modification of fluoropolymers such as poly(tetrafluoroethylene) (PTFE) has been of importance in their industrial utilization.[1] Recently, there has been enhanced interest in photophysical[2] and/or photochemical[3,4] surface processing of fluoropolymers with a laser beam instead of the treatment with alkali metal in liquid ammonia or plasma discharge[1] for reasons of facility in operation and spatial controllability. However, little information has been given about the surface reaction or mechanistic features involved therein. The present communication describes a laser-induced photochemical reaction of fluoropolymers making their surfaces wettable through formation of a carboxylic group. We also found a clue to the mechanism of the surface photoreaction, where photoionization of liquid water followed by capture of a hydrated electron by the polymer was strongly suggested.

A poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) film (50-μm thickness) was fixed in contact with nitrogen-purged water in a cell sealed with quartz windows. The film was irradiated with an ArF laser (193 nm; 10 Hz; 22 mJ cm^{-2} pulse^{-1}; beam size 10−14 × 10−25 mm) for 2−17 min through the window. The contact angle of the FEP film with the water droplet (pH 6.5 ± 0.3) decreased with the increase of the shot number of the laser pulses from 107° before irradiation up to 40−50° (Figure 1). On the other hand, irradiation without water or immersion of the film in water in the dark did not affect the surface properties. Little topographic change before and after the irradiation was observed by scanning electron microscopy which ruled out surface roughness induced by laser ablation as an origin of the wettability. The wettability was attributed to the formation of carboxylic groups at the surface by the following observations: (i) X-ray photoelectron spectroscopy (XPS) indicated the appearance of a component attributable to the carbonyl group at 286−290 eV in the C_{1s} region, loss of fluorine (F/C atom from 2.3 to 0.6−1.2), and an increase of oxygen (O/C ratio from 0.02 to 0.10−0.20). (ii) Basic or cationic dyes such as rhodamine 6G or acid violet 17 and not anionic dyes such as eosin Y absorbed onto the irradiated surface from their aqueous solutions.[7] The absorbance (A) at 540 nm based on rhodamine 6G adsorbed at the surface increased with the increase of shot number, as shown in Figure 1. (iii) In the contact angle titration with buffer droplets,[6] the contact angle decreased from 63° to 59° by changing the pH from 6.9 to 9.2. The quantity of carboxylic groups at the surface was estimated semiquantitatively as a surface coverage of the dye (S) $S = A/1000\epsilon$, assuming that the molar extinction coefficient (ϵ) of adsorbed rhodamine 6G at 540 nm is the same as that in water ($\epsilon = 1 \times 10^5$ M^{-1} cm^{-1}). For 5000 pulses, $A = 0.017$ in Figure 1, the surface coverage was 1.7×10^{-10} mol cm^{-2} (1.0 molecule nm^{-2}).

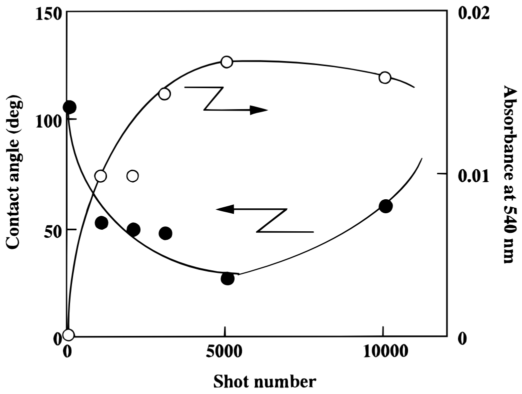
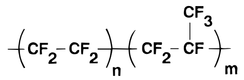
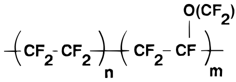


Figure 1. Plot of the contact angle of the irradiated FEP films with the water droplet (closed circle) and absorption at 540 nm based on the adsorption of rhodamine 6G (open circle) versus the shot number of the ArF laser pulse (22.9 mJ cm^{-2} pulse^{-1}).

Table 1. Surface Wettability of Fluoropolymers Irradiated through a 100-μm Water Film by the Use of Various Light Sources

Polymer	(Contact angle before irradiation (deg))	Contact angle after irradiation (deg) 185 nm[a]	193 nm[b]	248 nm[c]	254 nm[d]
 $\left(\mathrm{CF_2-CF_2}\right)_n\left(\mathrm{CF_2-}\overset{\mathrm{CF_3}}{\overset{\mid}{\mathrm{CF}}}\right)_m$ FEP	(107)	52	56	57	107
$\left(\mathrm{CF_2-CF_2}\right)_n$ PTFE	(119)	48	43	57	119
 $\left(\mathrm{CF_2-CF_2}\right)_n\left(\mathrm{CF_2-}\overset{\mathrm{O(CF_2)_kF}}{\overset{\mid}{\mathrm{CF}}}\right)_m$ PFA	(107)	46	48	60	107
$\left(\mathrm{CF_2-CF_2}\right)_n\left(\mathrm{CH_2-CH_2}\right)_m$ ETFE	(101)	66	77[e]	80[e]	101
$\left(\mathrm{CF_2-CH_2}\right)_n$ PVDF	(84)	75[e]	84[e]	98[e]	84

[a] 30-W super low-pressure Hg lamp (1 mW cm^{-2}), 60 min. [b] ArF laser (22 mJ cm^{-2} pulse^{-1}, 3000 shots). [c] KrF laser (68 mJ cm^{-2} pulse^{-1}, 3000 shots). [d] 60-W low-pressure Hg lamp with a 3-cm thick water filter (2.2 mW cm^{-2}), 4 h. [e] Polyene formation was observed.

Thin films (50−200 μm) of fluoropolymers of various fluorine contents were irradiated with various light sources, as summarized in Table 1. Irradiation of FEP films in contact with water under nitrogen at 185 nm with a 30-W super-low-pressure Hg lamp for 10−70 min also made the surface wettable, but not at 254 nm (60 W, low-pressure Hg lamp, 4 h). Irradiation with a KrF

S0024-9297(94)06441-7 CCC: $12.00

laser (248 nm; 50–150 mJ cm^{-2} $pulse^{-1}$) effectively afforded the wettable surface as obtained by an ArF laser or 185-nm irradiation. Similar results were obtained for highly fluorinated polymers such as PTFE or poly(perfluoroalkyl vinyl ether-*co*-tetrafluoroethylene) (PFA). However, hydrogen-containing polymers such as poly(ethylene-*co*-tetrafluoroethylene) (ETFE)[8] and poly(vinylidene fluoride) (PVDF), for which electron affinities lower than those of perfluoropolymers are expected owing to the electron-donating nature of the ethylene or methylene unit and the short chain of the electron-withdrawing CF_2 unit,[8,10] were less reactive to water with any light sources. The polymer effect strongly suggests that the present photoreaction is ruled by electron affinity of the polymers and not by reactivity toward radicals.[10,11]

The effects of oxygen and light sources suggest an incorporation of a hydrated electron as a key intermediate. When FEP films were irradiated at 193 nm with aerated water, the contact angle decreased only a little. The photoreaction was completely suppressed by saturation of water with oxygen. The quantities of dye-adsorption onto the films irradiated under aerated conditions were 1/10 to 1/30 of that under nitrogen at the same laser intensity. We obtained the lifetime of the hydrated electron to be 2–5 μs by the Stern–Volmer treatment assuming the presence of a hydrated electron as a key intermediate and a quenching rate by oxygen of 2.2×10^{10} M^{-1} s^{-1}.[12] The present result is almost in good accordance with the reported value of 1–2 μs.[13] PTFE has no absorption at >180 nm, whereas water has an onset of absorption around 190–200 nm.[14] Essentially, this will be the same for other fluoropolymers and excitation of water can be expected for the irradiation at 185 and 193 nm. At these wavelengths, the photon energies exceed the threshold of one-photonic ionization of liquid water (6.0–6.5 eV, 191–207 nm in wavelength),[15,16] whereas only multiphotonic ionization with intense laser pulses is allowed for wavelengths longer than the threshold. Therefore, this explains the results obtained with the KrF laser and the low-pressure mercury lamp.

The laser-intensity dependence of the reaction was studied to estimate the number of photons involved therein. Since a quantity (Q) caused by multiphotonic excitation is generally expressed in the form $Q = A\sigma I^n$ (A, constants; σ, the absorption cross section; I, the laser intensity; n, the number of photon ($n \geq 1$)), a double logarithmic plot of Q against I will show a linear relationship with a slope of n. The quantities of carboxylic groups formed per pulse estimated by the dye adsorption at initial stages of the reaction performed with ArF and KrF lasers of various pulse intensities were plotted on a double-logarithmic scale (Figure 2). The plots were fitted by the straight lines with slopes of 1.4 ± 0.2 and 3.2 ± 0.5 for ArF and KrF lasers, respectively. The slopes in Figure 2 larger than 1 and 2, which are expected for formation of a hydrated electron with ArF and KrF lasers,[13] suggested that the carboxylic group is formed not only by photoionization of water but also by a secondary photoreaction.[17] A possible mechanism for the present surface photoreaction is depicted in eqs 1–8: photoionization of water (1); capture of a hydrated electron by the fluoropolymer (2); elimination of a fluoride ion from the fluoropolymer radical anion (3 and 4); attack of the •OH radical on the radical site on the polymer (5 and 6); elimination of HF from alcohols giving a carboxylic or ketone group (7 and 8).

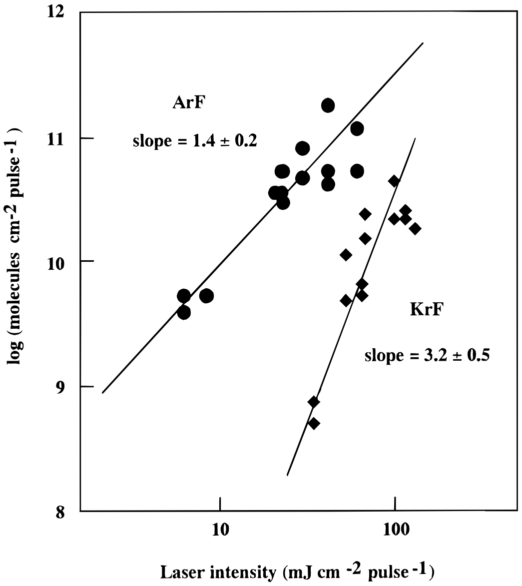


Figure 2. Laser-power dependence of the rhodamine 6G adsorption on FEP films irradiated with ArF and KrF lasers in contact with N_2-purged water.

$$H_2O \xrightarrow{h\nu \text{ or } 2h\nu} H^+ + {}^\bullet OH + e_{aq}^- \tag{1}$$

$$\text{fluoropolymer} + e_{aq}^- \rightarrow (\text{fluoropolymer})^{\bullet -} \tag{2}$$

$$(\text{fluoropolymer})^{\bullet -} \rightarrow -\dot{C}F- \text{ (on chain)} + F^- \tag{3}$$

$$(\text{fluoropolymer})^{\bullet -} \rightarrow -CF_2^{\bullet} \text{ (at termini)} + F^- \tag{4}$$

$$-\dot{C}F- + {}^\bullet OH \rightarrow -CF(OH)- \tag{5}$$

$$-CF_2^{\bullet} + {}^\bullet OH \rightarrow -CF_2OH \tag{6}$$

$$H_2O + -CF_2OH \rightarrow -COOH + 2HF \tag{7}$$

$$-CF(OH)- \rightarrow -CO- + HF \tag{8}$$

As a conclusion, the photoreaction of the fluoropolymer surface with water is essentially similar to the reactions with several electron-donating species.[1,20–22] The single electron transfer mechanism will provide a key principle in designing photochemical modification of the fluoropolymer surface.

Supporting Information Available: An illustration of cell structure for the irradiation, a table for the pH dependence of the contact angle, and XPS spectra of FEP films (original and irradiated with the ArF laser in contact with water) (3 pages). Ordering information is on any current masthead page.

References and Notes

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(8) An alternating structure of ethylene and tetrafluoroethylene units was supported by the XPS C_{1s} spectrum.[9]

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(10) PTFE and large perfluoroalkanes show an electrochemical activity toward reduction, see: Barker, D. J.; Brewis, D. M.; Dahm, R. H. *Electrochim. Acta* **1978**, *23*, 1107. Marsella, J. A.; Gilicinski, A. G.; Coughlin, A. M.; Pez, G. P. *J. Org. Chem.* **1992**, *57*, 2856.

(11) Irradiation of the fluoropolymer films with a 3% H_2O_2 aqueous solution did not improve the wettability, and no adsorption of rhodamine 6G on the irradiated surface was observed. This rules out simple attack of the hydroxyl radical on the polymer surface.

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