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ESR Study and Surface Reaction of Laser-Ablated Polymer Films

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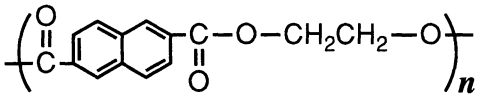
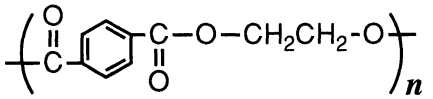
The formation of radicals on the surface of poly(ethylene naphthalate) (PEN) and poly(ethylene terephthalate) (PET) films after KrF excimer laser ablation was investigated by electron spin resonance (ESR) measurement and by surface immobilization reaction with an acrylic acid ester and a styrene derivative at a cryogenic temperature. The ESR spectrum of ablated PEN film in a sealed quartz tube shows a broad singlet-like peak.

Excimer laser ablation of polymer films has been shown to be useful for etching and surface modification.[1-3] Recently, we have investigated the ionic (electrostatic) behavior of a laser-ablated polymer surface with a surface potential meter.[4,5] On the basis of these studies, it is assumed that transient radicals and ions are formed on the surfaces in the course of ablative photodecomposition by the UV laser irradiation. The properties of radicals on the ablated polymer surface is still an open question, although the chemical composition of the surfaces has been analyzed by X-ray photoelectron spectroscopy (XPS)[6,7] and infrared spectroscopy.[8] In the present study, we report the formation of radicals on the surface of polyester films by KrF excimer laser ablation. In addition, we also investigated the chemical reactivity of the intermediates with such vinyl monomer as an acrylic acid ester and a styrene derivative under a cryogenic atmosphere.

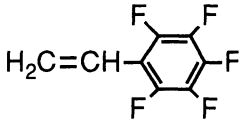
The radiation apparatus used for the experiments was a KrF excimer laser at 248 nm (Lambda Physik, EMG-201MSC; pulse duration: *ca.* 30 ns).[7] Poly(ethylene naphthalate) (PEN; manufactured by Teijin Ltd.) and poly(ethylene terephthalate) (PET; Daia Foil Ltd.) films were 100 μm in thickness and free from magnetic impurities (Fig. 1). Electron spin resonance (ESR) [JEOL, JES-RE1X (X-band)] was used to detect the radicals of polyester films in a sealed capillary quartz tube (Nippon Seimitsu Kagaku Ltd., NES-1) under a vacuum (10^{-3} Pa) at 77 K and 300 K. The number of free radicals was estimated by the integration of a first derivative curve and by comparison with α,α'-diphenyl-β-picrylhydrazyl (DPPH; Tokyo Chemical Industry Co., Ltd.).



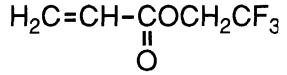
Poly(ethylene naphthalate) (PEN)



Poly(ethylene terephthalate) (PET)



Pentafluorostyrene (**1**)



Acrylic acid 2,2,2-trifluoroethyl ester (**2**)

Fig.1. Chemical structures of polyesters and vinyl monomers.

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Pentafluorostyrene (**1**) and acrylic acid 2,2,2-trifluoroethyl ester (**2**) (from T.C.I.) in Fig.1 were used for surface reaction in a cryostat (Toyo Sanso Ltd., TC-115FB). The immobilization of these monomers having fluorine atoms onto the surfaces through a chemical bond was confirmed by XPS. XPS analysis was performed on a surface analyzer (VG Scientific Ltd., ESCA LAB Mark2) using Mg-Kα radiation without a monochromator.

Figure 2 shows the ESR spectrum of PEN film ablated with a KrF excimer laser at the fluence of 140 mJ•cm^{-2} with 10 shots in a sealed capillary tube at 77 K.[9] The ESR spectrum had a broad singlet-like peak with the g-value of 2.0026, suggesting that free radicals of *ca.* 4 spins• nm^{-2} were formed at an immobilized dangling-bond site of carbon atoms.[10,11] Although the radicals were stable in the sealed tube at 300 K, 70% of radicals disappeared on the film by exposure to ambient air (Fig.3). The shape of ESR spectra after exposure to air was almost the same as that before, indicating that no new species were formed on the surface by the exposure. The 30% of radicals on the film was stable for several days in the ambient air.

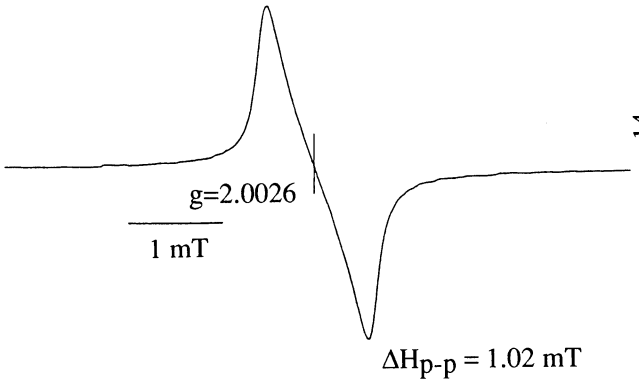

Fig.2. ESR spectrum of ablated PEN film in a sealed quartz tube at 77 K (KrF laser, 140 mJ•cm^{-2}, 10 shots).

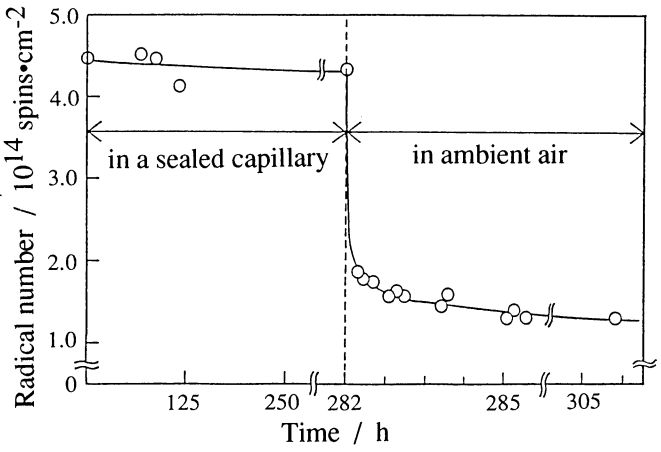

Fig.3. The number of free radicals on ablated PEN film in a sealed capillary and in ambient air at 300 K.

When a PET film was ablated with KrF laser at the fluence of 125 mJ•cm^{-2} with 10 shots in the tube at 77 K, two broad signals due to an aromatic radical (*p*-C_6H_3•)[12] and the dangling-bond sites were observed in an ESR spectrum. The radicals of ablated PET film, whose population was lower than that of the PEN film, were unstable in the tube when the temperature was raised up to 300 K. The difference in the stability of these radicals can be ascribed to molecular motions of the polymer chain, since the surface layer of ablated PET film consists of oligomers[6] while ablated PEN surface has cross-linked molecules[7] whose motions are restricted. Since hyper-fine structures in these ESR spectra were hardly discernible, the chemical structure of radicals on the films was not proved precisely.

On the basis of the behavior of radicals on the ablated films, we investigated the surface reaction of the films with styrene and acrylic acid derivatives under a cryogenic atmosphere. The reaction procedure consists in three steps (Fig.4). First, the polyester films cast on a sapphire plate was ablated in a cryostat at 83 K (6×10^{-4} Pa) using a KrF excimer laser (150 mJ•cm^{-2}, 15 shots). Second, the vapors of styrene (**1**) or acrylic

acid ester (**2**) were adsorbed on the ablated surface at 83 K. Finally, the temperature of the sample film was raised up to 300 K to eliminate unreacted **1** or **2** from the surface.

The surface of the PEN and PET films ablated with the KrF excimer laser showed chemical reactivity with **1** and **2**. When the ablated PEN surface was treated with **1**, the surface coverage of **1** was estimated to be 1.4 molecule•nm^{-2} by the calculation from the area of F_{1s} peak of **1** in the XPS spectrum of the treated PEN film (Fig.5).[13] No F_{1s} peak in XPS was detected on the unirradiated surface of PEN film, as expected. In the case of **2**, the monomer of *ca.* 19 molecule•nm^{-2} was grafted on the ablated PEN film. On an ablated PET surface by KrF laser irradiation at 150 mJ•cm^{-2} with 25 shots at 85 K, **1** was also immobilized (*ca.* 2.3 molecule•nm^{-2}). The chemical reactivity on the ablated surface is mainly attributed to the reactive sites having radicals, because the amount of the immobilized monomers is comparable to that of radicals detected by ESR.

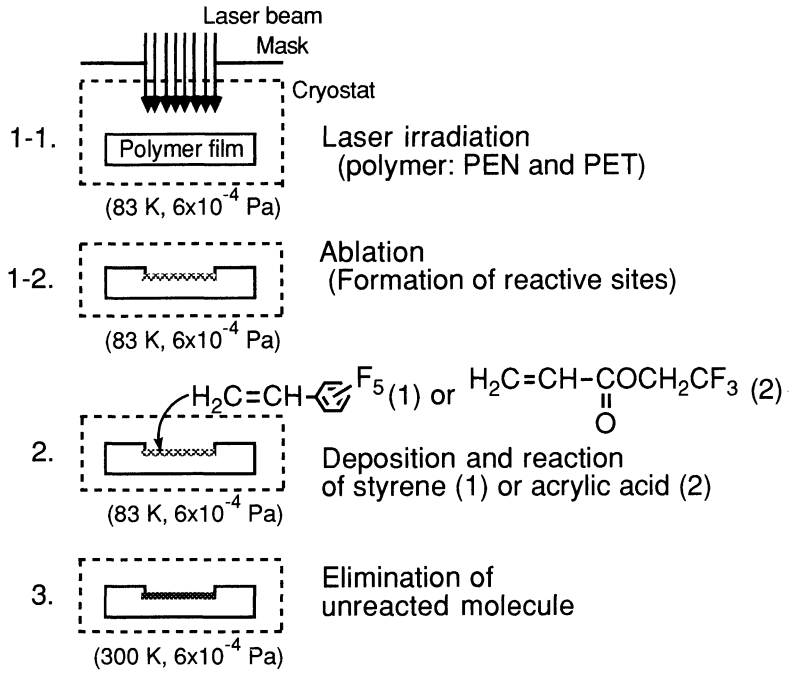

Fig.4. Schematic diagram on the surface reaction of laser-ablated polyester films with pentafluorostyrene (**1**) or acrylic acid 2,2,2-trifluoroethyl ester (**2**) under a cryogenic atmosphere.

In addition, the chemical reactivity with **1** and **2** was also checked on the surface of a thin solid film produced by the deposition of fragments in KrF laser ablation of the polymers. After the fragments ejected from PEN film (150 mJ•cm^{-2}, 100 shots) was deposited on a glass plate in a reaction vessel under a vacuum (10^{-3} Pa) at 300 K, the vessel was filled with the monomer vapors up to their saturation vapor pressure at 300 K. The monomers **1** and **2** of 5.8 and 4.3 molecule•nm^{-2}, respectively, were immobilized on the deposited film for the surface reaction of radicals detected by ESR.

We first demonstrate that transient radicals which was detected by ESR at a cryogenic temperature exist on the polyester surface after excimer laser ablation, although it is reported that C_2 and CN radicals are confirmed in ablated fragments from a polyester surface.[14] Owing to the chemical reactivity of radicals, the vinyl monomers

can be polymerized on the ablated films without any subsequent photo-irradiation. These results would be useful for surface modification of polymer film in industrial applications.

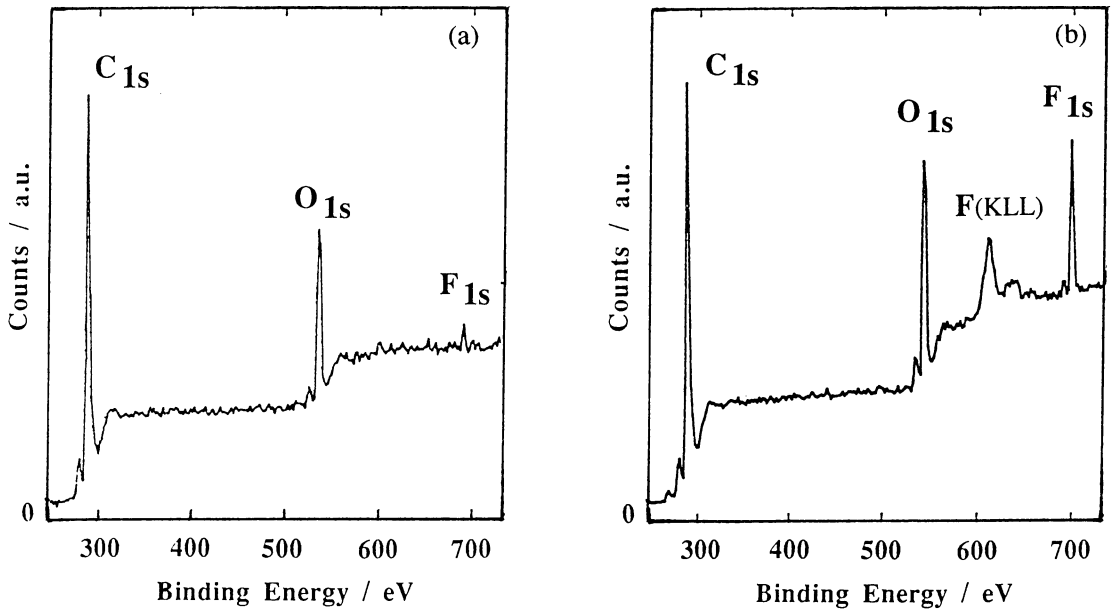

Fig.5. XPS spectra of PEN film; (a) after the treatment of styrene (**1**), (b) after the treatment of acrylic acid (**2**).

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13) The analytical depth of polymer surface for XPS is estimated to be 10 nm. Atomic sensitivity of C : O : F for XPS is 0.205 : 0.63 : 1.00.
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