

Hydrophobic Polymer Films Plasma-Polymerized from CF₄/Hydrocarbon and Hexafluoroacetone/Hydrocarbon Mixtures

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SYNOPSIS

Polymer films were deposited from the plasma polymerization of the mixtures of hydrocarbons, ethane, ethylene, and acetylene, and tetrafluoromethane (CF₄) or hexafluoroacetone (HFA). The surface properties, the advancing contact angle of water, and surface energy of the films deposited and the chemical composition at the outermost layer of the films are discussed from the data of the angular XPS measurements. The plasma polymers deposited from the CF₄/hydrocarbon and HFA/hydrocarbon mixtures contained fluorine atoms whose content depended on the CF₄ or HFA concentration of the mixtures. The hydrophobicity of the films deposited could not be determined by the fluorine content of the films but by the chemical composition of the fluorine moieties at the outermost layer of the films. The CF₃ moieties rather than the CF₂ and CF moieties contribute largely to the hydrophobicity of the films. The plasma polymer films deposited from the HFA/acetylene (87.5 mol % HFA) showed higher hydrophobicity (the surface energy is 9.7 mJ/m²) than those from the CF₄/acetylene mixture (87.5 mol % CF₄) (the surface energy is 13 mJ/m²).

INTRODUCTION

Hydrophobic polymer surfaces potentially call for water-repellancy, nonstickness, blood compatibility, and wax-free coating for painted surfaces.¹ For that aim, fluoro polymers are frequently used because of their high hydrophobicity. A successive process, a coating process of fluoro polymer emulsion and a curing process of the fluoro polymer, is employed commercially for the formulation of hydrophobic surfaces.¹ Instead of the coating process, the surface fluorination of polymer substrates and the deposition of fluorine polymers onto polymer surfaces have been focused on.²⁻¹³ The two processes have an advantage of hydrophobic surface modification without affecting the bulk properties of the polymer substrates. The surface fluorination, in the chemical sense, is a substitution reaction of hydrogen in the polymer substrates with fluorine atom. Fluorine gas activated by ultraviolet light and fluorine compounds such as CF₄, C₂F₆, and SF₆ activated by plasma are

used as reagents for the direct fluorination reaction.²⁻¹⁰ The polymer deposition process, which is called plasma polymerization, is a thin-film process of fluoro polymers, which occurs at the surface of the polymer substrates. Fluorine-containing, unsaturated, or ring monomers such as tetrafluoroethylene, hexafluoropropene, and perfluorobutyltetrahydrofuran are plasma-polymerized by the action of plasma, and the plasma polymers deposit on the surface of the polymer substrates.¹⁴⁻¹⁷

In the practice of surface modification, we should direct attention to how hydrophobic the surface of the polymer substrates was modified and to how durable it was. Hydrophobic moieties present at the air/polymer interface move away from the surface into the bulk of the polymer when the polymer faces are exposed to humid atmosphere or are immersed into water.¹² In this sense, the surface fluorination of polymers, especially linear polymers, is not an adequate technique for hydrophobic modification. Plasma polymers are composed of highly cross-linked polymer chains. Accordingly, with the rotational and diffusional movement of the hydrophobic moieties being present, the air/polymer interface could be restricted. In this sense, the polymer de-

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position process by plasma polymerization is effective in durability.¹⁸

In this study, the formation of hydrophobic polymer films by the plasma polymerization of fluoro compounds and surface properties of the films deposited were investigated. Tetrafluoromethane (CF₄) and hexafluoroacetone (HFA), instead of unsaturated fluoro compounds such as tetrafluoroethylene and hexafluoropropene, were used as starting materials for the plasma polymerization. CF₄ and HFA give no plasma polymers when excited by the action of plasma. The two fluorine compounds, however, give some polymers in which the polymer chains are extremely cross-linked when plasma-polymerized in the presence of hydrocarbons. In such a mixture system, polymer films will be highly cross-linked and are expected to be effective in the durability of hydrophobicity. Plasma polymerization of the CF₄/ethane, CF₄/ethylene, CF₄/acetylene, HFA/ethane, HFA/ethylene, and HFA/acetylene mixtures were investigated as a function of the CF₄ or HFA concentration.

EXPERIMENTAL

Plasma Polymerization

A handmade reactor that was inductively coupled with a radio-frequency (rf) (13.56 MHz) generator (Nihon Koshuka Co., Japan, model SKN-05P, max power 500 W) was used in this study for plasma polymerization. It consisted of a Pyrex glass tube (100 mm inner diameter and 605 mm long, volume 3241 cm³) with a monomer inlet at a distance of 210 mm from the end of the reactor, a pressure gauge at 105 mm, and a coil (six turns) for inductive coupling of the rf power at the end of the reactor. The other end of the reactor was connected to a vacuum system (a combination of rotary and diffusion pumps). A low-density polyethylene sheet (10 × 30 mm × 30 μm thick) or aluminum foil (5 × 22 mm × 5 μm thick) used as substrates for plasma polymer deposition were mounted on a glass plate with double-side adhesive tape and were positioned horizontally in the Pyrex glass reactor. The details of the reactor have been given elsewhere.¹⁸

The experimental procedures for the plasma polymerization were essentially the same as reported elsewhere.¹⁸ The reaction system was evacuated to approximately 0.13 Pa, and, then, monomer gases (mixtures of tetrafluoromethane and hydrocarbons or those of hexafluoroacetone and hydrocarbons), adjusted to a flow rate of 4 cm³ (STP)/min at 1.3

Pa, were introduced into the reaction chamber. The plasma polymerization was continued at an rf power of 25 W for 30 min. The polymer deposition rate (in μg/cm² min) from the plasma polymerizations of these mixtures was measured from the weight change of the aluminum foils before and after the plasma polymerization.

Tetrafluoromethane (CF₄) (99.99% purity, purchased from Takachiho Trading Co.), hexafluoroacetone (HFA) (99.9% purity, supplied kindly from the Central Glass Co.), ethane (99.9% purity, purchased from Takachiho Trading Co.), ethylene (99.9% purity, purchased from Takachiho Trading Co.), and acetylene (99.9% purity, purchased from Takachiho Trading Co.) were used.

Fourier Transform Infrared Spectra of Deposited Plasma Films

Attenuated total reflection (ATR) IR spectra for the plasma films deposited on the polyethylene sheet surface were recorded on a Nihon Bunko Fourier transform spectrometer FT/IR-3. The crystal of KRS-5 was used for attenuated total reflection. The purity of the crystal surface was monitored before each analysis by recording a spectrum of the bare crystal. The incidence angle of infrared light was 45°. The sampling depth, which is a function of the infrared wavelength, the reflective index¹⁹ (2.4 for KS-5 crystal, 1.4–1.6 assumed for the composite of the plasma polymers and polyethylene layers), and the incidence angle of infrared light (45°), is calculated to be about 0.5–12 μm in the wavelength range of 2.5 to 25 μm. The spectral resolution was 2 cm⁻¹, and 1000 scans were recorded on each sample.

XPS Spectra

XPS spectra for the plasma films deposited on the polyethylene sheet surface were obtained on an Ulvac-Phi spectrometer model 5300 using an AlKα photon source (a voltage of 15 kV, a wattage of 400 W, and a background pressure of 1 × 10⁻⁷ Pa) as a function of the takeoff angle (θ) (15, 30, 45, and 75°). The takeoff angle (θ) is defined as the angle between the sample surface and the XPS energy analyzer. The sampling depth (*l*) is calculated from the equation $l = 3\lambda \sin \theta$ (Ref. 19) to be 25, 50, 70, and 96 Å under an assumption of an escape depth (λ) of 100 Å. The C_{1s} spectra were deconvoluted by fitting five Gaussian functions to the experimental curve using a nonlinear, least-square curve-fitting program supplied by Ulvac-Phi. The following sen-

sitivity factors (S) for core levels were used to calculate the relative atomic concentration on surfaces of the plasma films: $S(C) = 1.00$, $S(F) = 4.00$, and $S(O) = 2.64$.

Advancing Contact Angle of Water and Surface Energy

The advancing contact angle of the water and the surface energy are indicators of the hydrophobicity of the deposited plasma films. The contact angle was measured at 25°C with an Erma microscopic goniometer model G-I. Test liquids were twice-distilled water, glycerol, formamide, diiodomethane, and tricresyl phosphate (analytical grade, purchased from Tokyo Kasei Kogyo, Japan) for the estimation of the surface energy. The contact-angle measurements were performed within 10 min after finishing the plasma polymerization to avoid the aging of the plasma polymer surfaces. The contact-angle data were analyzed to determine the surface energy according to Kaelble's method.²⁰

RESULTS AND DISCUSSION

Polymer Deposition Rate in Plasma Polymerizations of CF_4 /Hydrocarbon and HFA/Hydrocarbon Mixtures

Plasmas of tetrafluoromethane (CF_4) and hexafluoroacetone (HFA) give no polymer deposition but give some deposition of fluorine-containing polymers when hydrogen sources such as hydrocarbons and polyethylene are introduced into the plasmas. In such systems, CF_4 and HFA are useful fluorinating reagents in plasma polymerization. The mechanism of the polymer deposition process in the plasma polymerization of the CF_4 /hydrocarbon mixtures has been explained by Yasuda²¹ from the point of view of the bond strength of F—F and F—H bonds. In this study, ethane, ethylene, and acetylene were chosen as hydrogen sources for the assistance of the plasma polymerization of CF_4 and HFA. From the point of view of the polymer deposition, the plasma polymerizations of CF_4 /hydrocarbon mixtures, CF_4 /ethane, CF_4 /ethylene, and CF_4 /acetylene mixtures, and those of HFA/hydrocarbon mixtures, HFA/ethane, HFA/ethylene, and HFA/acetylene mixtures, were discussed. The polymer deposition rate in these plasma polymerizations showed strong dependence on the kind of the hydrocarbons and the CF_4 or HFA concentration. Figure 1(a) shows the polymer deposition rate in the plasma polymeriza-

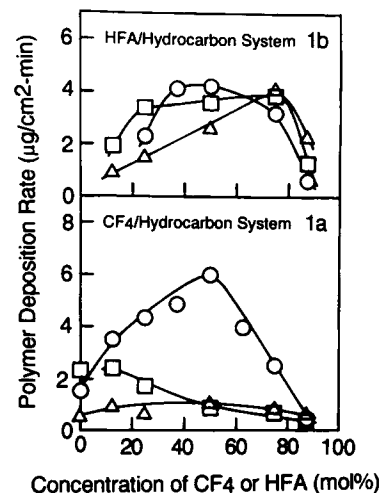


Figure 1 Polymer deposition rate in plasma polymerization of CF_4 /ethane (Δ), CF_4 /ethylene (\square), and CF_4 /acetylene (\circ) mixture systems (a) and in plasma polymerization of HFA/ethane (Δ), HFA/ethylene (\square), and HFA/acetylene (\circ) mixture systems (b) as a function of CF_4 or HFA concentration.

tion of the CF_4 /ethane, CF_4 /ethylene, and CF_4 /acetylene mixtures as a function of the CF_4 concentration. In the plasma polymerization of the CF_4 /ethane mixtures, the polymer deposition rate increases slightly from 0.94 to 1.06 $\mu\text{g}/\text{cm}^2 \text{ min}$ with an increase of the CF_4 concentration from 0 to 50 mol %. In the plasma polymerization of the CF_4 /ethylene mixtures, the deposition rate decreases linearly from 2.3 to 0.26 $\mu\text{g}/\text{cm}^2 \text{ min}$ with an increase of the CF_4 concentration from 0 to 87.5 mol %. Contrarily, the polymer deposition rate in the plasma polymerization of the CF_4 /acetylene mixtures increases with an increase of the CF_4 concentration and reaches a maximum (6.1 $\mu\text{g}/\text{cm}^2 \text{ min}$) at a CF_4 concentration of 50 mol %. The plasma polymerization of the CF_4 /acetylene mixtures deposits the plasma polymer films at the fastest polymer deposition rate of the three polymerizations.

Similarly, the plasma of hexafluoroacetone (HFA) also could interact with hydrocarbon molecules and gives the deposition of plasma polymers containing fluorine atoms. Figure 1(b) shows the polymer deposition rate in the plasma polymerization of the HFA/ethane, HFA/ethylene, and HFA/acetylene mixtures as a function of the HFA concentration. In the plasma polymerization of all the three mixtures, the polymer deposition rate is increased by mixing HFA molecules and reaches maximum deposition rates of 4.17, 3.86, and 4.25 $\mu\text{g}/\text{cm}^2 \text{ min}$ in the plasma polymerizations of the HFA/ethane (at 75 mol % HFA), HFA/ethylene (75 mol

% HFA), and HFA/acetylene mixtures (50 mol % HFA), respectively. Comparison between Figure 1(a) and (b) shows that the plasma polymerizations of the HFA/hydrocarbon mixtures give plasma polymers at faster deposition rates than do the plasma polymerizations of the CF_4 /hydrocarbon mixtures. From the viewpoint of the polymer formation, HFA is a suitable monomer for the deposition of fluorine-containing plasma polymers other than CF_4 .

Advancing Contact Angle of Water and Surface Energy of Plasma Polymer Films Prepared from CF_4 /Hydrocarbon and HFA/Hydrocarbon Mixtures

Figure 2 shows the advancing contact angle of water on the surface of the plasma polymer films prepared from the CF_4 /ethane, CF_4 /ethylene, and CF_4 /acetylene mixtures and their surface energy as a function of the CF_4 concentration. Influences of the CF_4 mixing on the advancing contact angle of water appear at CF_4 concentrations of more than 50 mol %. The value of the advancing contact angle of water initiates an increase near the CF_4 concentration of 50 mol %, and the increase continues with increasing CF_4 concentration. When the CF_4 concentration increases from 50 to 87.5 mol %, the value of the advancing contact angle of water increases from 95 to 105° for the plasma polymer films prepared from the CF_4 /ethane mixture, from 90 to 104° for the

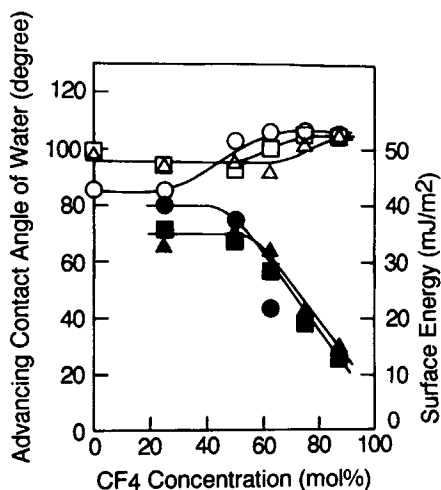


Figure 2 Advancing contact angle of water (open symbols) and surface energy (closed symbols) of plasma polymer films prepared from CF_4 /ethane (Δ), CF_4 /ethylene (\square), and CF_4 /acetylene mixtures (\circ) as a function of CF_4 concentration.

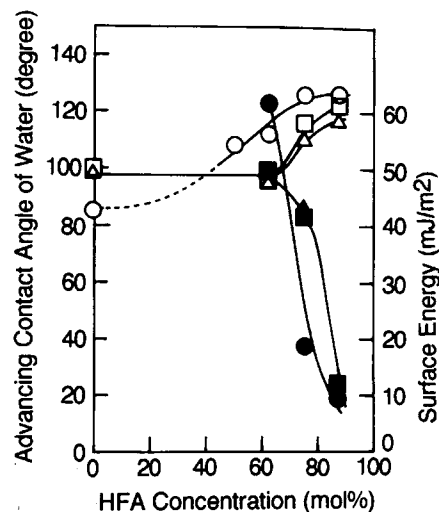


Figure 3 Advancing contact angle of water (open symbols) and surface energy (closed symbols) of plasma polymer films prepared from HFA/ethane (Δ), HFA/ethylene (\square), and HFA/acetylene mixtures (\circ) as a function of HFA concentration.

plasma polymer films prepared from the CF_4 /ethylene mixture, and from 103 to 106° for the plasma polymer films prepared from the CF_4 /acetylene mixture. At a CF_4 concentration of 87.5 mol %, the magnitude of the surface energy is 15.3, 14.5, and 13.0 mJ/m^2 for the plasma polymer films prepared from the CF_4 /ethane, CF_4 /ethylene, and CF_4 /acetylene mixtures, respectively. This figure indicates that hydrophobic polymer films whose advancing contact angle of water reaches more than 100° deposit from the plasma polymerization of the CF_4 /hydrocarbon mixtures, especially of those containing CF_4 concentrations of more than 50 mol %, and that surface properties, the advancing contact angle, and surface energy of the plasma polymer films depend on the CF_4 concentration of the CF_4 /hydrocarbon mixtures.

The plasma polymerization of the HFA/hydrocarbon mixtures also deposits hydrophobic films. Figure 3 shows the advancing contact angle of water on the plasma polymer films prepared from the HFA/ethane, HFA/ethylene, and HFA/acetylene mixtures. The contact angle increases with increasing HFA concentration, and then at an HFA concentration of 87.5 mol %, it reaches 117, 122, and 126° for the plasma polymer films prepared from the HFA/ethane, HFA/ethylene, and HFA/acetylene mixtures, respectively. Their surface energy at an HFA concentration of 87.5 mol % is 11.1, 12.0, and 9.7 mJ/m^2 for the plasma polymer films pre-

pared from the HAF/ethane, HFA/ethylene, and HFA/acetylene mixtures, respectively. By comparing Figures 2 and 3, we conclude that (1) the plasma polymerizations of the CF_4 /hydrocarbon and HFA/hydrocarbon mixtures give hydrophobic films, (2) the hydrophobicity of the films deposited depend on the kind of the hydrocarbons as well as on the CF_4 or HFA concentration of the mixtures, (3) the plasma polymerization of the CF_4 /acetylene and HFA/acetylene mixtures give higher hydrophobic plasma polymer films whose surface energy is 13.0 and 9.7 mJ/m^2 , respectively, and (4) HFA makes the plasma polymer films deposited more hydrophobic than does CF_4 .

Chemical Composition of Plasma Polymers Prepared from CF_4 /Hydrocarbon and HFA/Hydrocarbon Mixtures

The hydrophobicity is considered to be determined mainly by the chemical composition of the plasma polymer films, especially the outermost layer of about 30 Å thick. The surface layer of the plasma polymer films was analyzed by ATR FTIR spectrometry and angular XPS. The plasma polymer films deposited from the plasma polymerization of the CF_4 /acetylene and HFA/acetylene mixtures were used as the specimens to be analyzed. The plasma polymer films deposited from the CF_4 /acet-

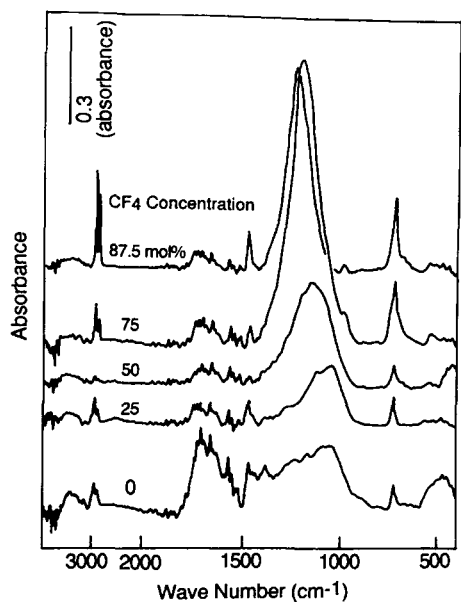


Figure 4 IR spectra of plasma polymer films prepared from CF_4 /acetylene mixtures as a function of CF_4 concentration.

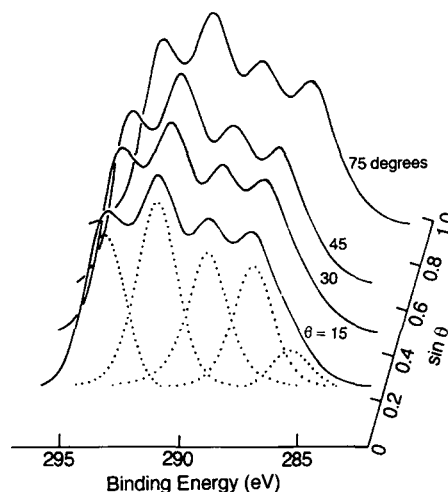


Figure 5 F/C and O/C atomic ratios for plasma polymer films prepared from CF_4 /acetylene containing CF_4 concentrations of 75 (Δ) and 87.5 mol % (\circ) and HFA/acetylene mixtures containing HFA concentrations of 75 (\blacktriangle) and 87.5 mol % (\bullet) as a function of takeoff angle ($\sin \theta$).

ylene and HFA/acetylene mixtures showed similar IR spectra. Figure 4 shows typical IR spectra of the films deposited from the acetylene/ CF_4 mixtures as a function of the CF_4 concentration. Strong absorption peaks due to C—F stretching vibration and CF_3 deformation vibration appear at 1230 and at 740 cm^{-1} , respectively, and absorption peaks due to C—H stretching vibration and C—H deformation vibration also appear at 2910, 2850, and 1460 cm^{-1} .²² At a CF_4 concentration of 87.5 mol %, the peak position of C—F stretching vibration shifts to higher wavenumber regions. This shift indicates the formation of CF_3 moieties.²² The intensities of the absorption peaks due to the C—F stretching vibration and CF_3 deformation vibration increase with increasing CF_4 concentration. The spectra suggest that the plasma films deposited contain fluorine atoms, that the concentration of fluorine atoms incorporated is increased with increasing CF_4 concentration of the CF_4 /acetylene mixtures, and that the incorporation of the fluorine atoms may be closely related to the hydrophobicity of the plasma polymer films.

The elemental composition of the plasma polymer films deposited was analyzed with XPS. Practically, the F/C and O/C atomic ratios of the outermost layer of the plasma polymer films were estimated from the data of the angular dependence of the XPS spectra. In XPS measurement, the effective sampling depth is proportional to the mean-free path of electron and inversely proportional to $\sin \theta$, where

Table I Elemental Composition Present at Outermost Layer of Plasma Polymer Films Prepared from CF₄/Acetylene and HFA/Acetylene Mixtures and Surface Energy

Monomer Mixture for Plasma Polymerization	CF ₄ or HFA Concentration (mol %)	Atomic Ratio at Outermost Layer		Surface Energy (mJ/m ²)
		F/C	O/C	
CF/acetylene	75	1.8	8.0 × 10 ⁻²	21.0
	87.5	2.2	2.0	13.0
HFA/acetylene	75	1.4	8.0	18.6
	87.5	1.5	3.6	9.7

θ is the takeoff angle of the photoelectron, which is defined as the angle between the sample and the energy analyzer. The relative intensity ratios of the F_{1s}/C_{1s} and O_{1s}/C_{1s} core levels, which means the F/C and O/C atomic ratios, were plotted against $\sin \theta$, and the F/C and O/C atomic ratios for the outermost layer of the plasma polymer films were estimated by the extrapolation of $\sin \theta = 0$ ($\theta = 0$ degrees). Figure 5 shows the F/C and O/C atomic ratios against $\sin \theta$ for the plasma polymer films prepared from CF₄/acetylene and HFA/acetylene mixtures containing CF₄ and HFA concentrations of 75 and 87.5 mol %. The four plasma polymers prepared from CF₄/acetylene and HFA/acetylene mixtures show less dependence of the F/C and O/C atomic ratios on the takeoff angle of the photoelectron. This indicates that the plasma polymer films deposited possess the homogeneous elemental composition in the range of at least the effective sampling depth (25–96 Å). Table I shows the F/C and O/C atomic ratios at the outermost layer, which were estimated by the extrapolation. The plasma polymers prepared from the CF₄/acetylene mixture have higher F/C atomic ratios at the outermost layer than do the plasma polymers from the HFA/acetylene mixtures. The value of the F/C atomic ratio is 2.2 and 1.8 for the plasma polymers prepared from the CF/acetylene mixtures containing CF₄ concentrations of 87.5 and 75 mol %, respectively, and 1.5 and 1.4 for the plasma polymers from the acetylene/HFA mixtures containing HFA concentrations of 87.5 and 75 mol %, respectively. The plasma polymers from the acetylene/HFA mixture containing an HFA concentration of 75 mol % possess the lowest F/C atomic ratio of 1.4. The value of the O/C atomic ratio for the four plasma polymers is negligibly low (2.0–8.0 × 10⁻²) compared with the F/C atomic ratio. From the results of the estimation, it is clear that the plasma polymerizations of the CF₄/acetylene and HFA/acetylene mixtures give plasma

polymers containing fluorine atoms and that the higher the CF₄ and HFA concentration of the CF₄/acetylene and HFA/acetylene mixtures are the higher the fluorine content of the plasma polymers deposited is. Also, more CF₄ molecules are incorporated into the plasma polymers deposited than are HFA molecules.

A relationship between the elemental composition at the outermost layer and the hydrophobicity of the plasma polymer films was discussed. The surface energy of the four plasma polymer films is tabulated in the fifth column in Table I. The plasma polymer films prepared from the CF₄/acetylene mixtures containing CF₄ concentrations of 75 and 87.5 mol % show surface energy of 21.0 and 13.0 mJ/m², respectively, and the polymers from the acetylene/HFA mixtures containing HFA concentrations of 75 and 87.5 mol % possess values of 18.6 and 9.7 mJ/m², respectively. From the comparison in Table

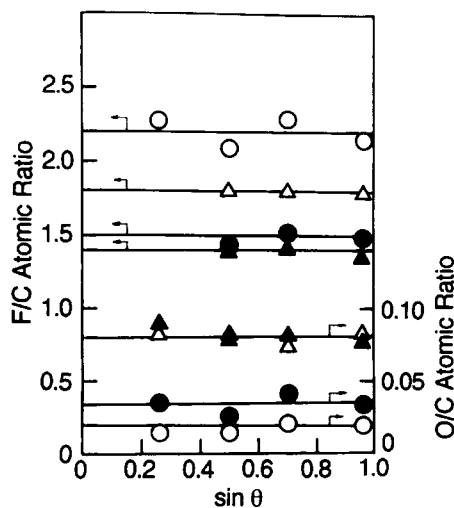
**Figure 6** XPS (C_{1s}) spectra for plasma polymer films prepared from CF₄/acetylene mixture (87.5 mol % CF₄) as a function of takeoff angle ($\sin \theta$).

Table II Relative Concentration of C_{1s} Components Present at Outermost Layer for Plasma Polymer Films Prepared from CF₄/Acetylene and HFA/Acetylene Mixtures

Monomer Mixture for Plasma Polymerization	CF ₄ or HFA Concentration (mol %)	Relative Concentration of C _{1s} Components (mol %)				
		CH—CF	CH—CF _n	CHF	CF ₂	CF ₃
CF ₄ /acetylene	75	19.1	26.4	22.7	17.9	14.0
	87.5	7.4	20.1	23.7	29.1	19.7
HFA/acetylene	75	26.1	23.6	17.1	15.2	18.0
	87.5	15.7	22.9	17.4	20.7	23.8

I, we observe no relationship between the F/C atomic ratio and the surface energy of the plasma polymer films. This suggests that the hydrophobicity of the plasma polymer films could not be determined by how much a concentration of fluorine atoms has been incorporated, but, instead, could be by what fluorine residues (chemical structure) have been incorporated into the plasma polymer films.

The plasma polymer films prepared from the CF₄/acetylene and HFA/acetylene mixtures showed similar C_{1s} core level spectra that contain five components: CH—CF at 286.4 eV, CH—CF_n at 287.8 eV, CHF at 289.3 eV, CF₂ at 291.5 eV, and CF₃ features at 294.0 eV.²³ Typical C_{1s} core level spectra for the plasma polymer films prepared from the CF₄/acetylene containing a CF concentration of 87.5 mol % are shown in Figure 6 as a function of the takeoff angle. From the angular dependence of the five C_{1s} components, the concentration of the five components at the outermost layer was estimated by the extrapolation of $\sin \theta = 0$. Table II shows the relative concentration of the five components at the outermost layer for the plasma polymer films prepared from the CF₄/acetylene and HFA/acetylene mixtures. The plasma polymer films prepared from the HFA/acetylene mixture containing an HFA concentration of 87.5 mol % show the highest CF₃ concentration (23.8 mol %), and the plasma polymer films from the acetylene/CF₄ mixture containing a CF₄ concentration of 75 mol % show the lowest CF₃ concentration (14.0 mol %). We can find out that there is a linear relationship between the CF₃ concentration at the outermost layer and the surface energy (Fig. 6). This relationship indicates that the CF₃ groups rather than CF₂ and CF groups at the outermost layer contribute mainly to hydrophobicity of the plasma polymer films. The importance of the chemical composition of the fluorine residues in hydrophobicity is pointed out. The CF₄/acetylene mixtures give plasma polymers rich in fluorine at-

oms, but their hydrophobicity is low. The HFA/acetylene mixture, however, deposits plasma polymers poor in fluorine atoms, but their hydrophobicity is high. This discrepancy may be due to the difference of the CF₃ concentration of the plasma polymer films, especially at the outermost layer. From the viewpoint of the chemical composition, we conclude that HAF is a more suitable reagent than is CF₄ to produce hydrophobic fluorine polymer films.

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REFERENCES

1. Y. Ikada, Ed., *Kobunshi Hyomen no Kiso to Ohyo* (in Japanese), Kagaku Dojin, Tokyo, 1986.
2. H. Schonhorn, P. K. Gallagher, J. P. Luongo, and F. J. Padder, Jr., *Macromolecules*, **3**, 800 (1970).
3. H. Shinohara, M. Iwasaki, S. Tsujimura, K. Watanabe, and S. Okazaki, *J. Polym. Sci. A-1*, **10**, 2129 (1972).
4. J. L. Margrave and R. J. Lagow, *J. Polym. Sci. Polym. Lett. Ed.*, **12**, 177 (1974).
5. D. T. Clark, W. J. Feast, W. K. R. Musgrave, and I. Ritchie, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 857 (1975).
6. M. Millard, J. Burns, and H. Sachdev, in *Physicochemical Aspects of Polymer Surfaces*, K. L. Mittal, Ed., Plenum, New York, 1983.
7. M. Strobel, S. Corn, C. S. Lyons, and G. A. Korba, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 1125 (1985).
8. M. Strobel, D. A. Thomas, and C. S. Lyons, *J. Polym. Sci. Polym. Chem. Ed.*, **25**, 3343 (1987).
9. M. Strobel, S. Corn, C. S. Lyons, and G. A. Korba, *J. Polym. Sci. Polym. Chem. Ed.*, **25**, 1295 (1987).
10. M. Strobel, C. S. Lyons, P. A. Thomas, M. C. Morgen, S. Corn, and G. A. Korba, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **42**, 73 (1988).

11. M. Kogama, K. Takahashi, T. Moriwaki, and S. Okazaki, *Nippon Kagaku Kaishi*, **1984**, 1719 (1984).
12. T. Yasuda, T. Okuno, K. Yoshida, and H. Yasuda, *J. Polym. Sci. Polym. Phys. Ed.*, **26**, 1781, 2061 (1988).
13. G. A. Corbin, R. E. Cohen, and R. F. Baddeur, *Macromolecules*, **18**, 98 (1985).
14. N. Inagaki and T. Nakanishi, *Polym. Bull.*, **9**, 390 (1983).
15. N. Inagaki and D. Tsutsumi, *Polym. Bull.*, **16**, 131 (1986).
16. H. Nomura, P. W. Kramer, and H. Yasuda, *Thin Solid Films*, **118**, 187 (1984).
17. N. Inagaki, S. Tasaka, and T. Murata, *J. Appl. Polym. Sci.*, **38**, 1869 (1989).
18. N. Inagaki, S. Tasaka, and Y. Takami, *J. Appl. Polym. Sci.*, **41**, 965 (1990).
19. Society of Polymer Science Japan, Eds., *Kobunshi no Hyomen Gijutsu* (in Japanese), Nikkan Kogyo Shinbunsha, Tokyo, 1987.
20. D. H. Kaelble, *Physical Chemistry of Adhesion*, Wiley, New York, 1971.
21. H. Yasuda, *Plasma Polymerization*, Academic Press, New York, 1985.
22. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1966.
23. D. T. Clark and W. J. Feast, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C12**, 191 (1975).

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