

# Preparation of Hydrophilic Plasma-Polymers Derived from Oxygen-Containing Organic Monomers

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## SYNOPSIS

Plasma polymerization of nine oxygen-containing organic monomers was surveyed for producing hydrophilic films on solid substrates on due consideration of chemical structures of the monomers, operative conditions for plasma polymerization, and resultant film characters. The wettability of the polymer films were evaluated by measuring the contact angles of water on the film surfaces while the power consumption was compared as the lowest wattage needed for sustaining normal deposition rates of the polymer films. It has been found that the monomers involving the triple bond in the chemical structure conducted plasma polymerization under very low wattage of radiofrequency power, and at the same time the deposition rate was relatively high. With respect to the chemical structures of the monomers, the hydroxyl group tended to initiate and sustain the electric discharge at somewhat lower power than other functional groups. Highly hydrophilic polymer films could, thus, be obtained under a soft plasma condition by using propargyl alcohol (2-propyn-1-ol) as a monomer having the triple bond and the hydroxyl group. X-Ray photoelectron spectra of the polymers suggested that the wettability was not simply dependent upon oxygen atom content of the polymers, but also dependent upon spatial arrangement of the oxygen atoms within the polymer molecules. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

A number of organic compounds have been tested as monomers for plasma polymerization, and those are classified into two groups, namely, monomers efficiently conduct polymerization and others significantly decompose within the discharge area.<sup>1-3</sup> According to the experiments reported so far, successful plasma polymerization was carried out using unsaturated hydrocarbon, halocarbon, and nitrogen-containing monomers, while oxygen-containing monomers were scarcely employed. Although oxygen-containing polymers were anticipated to display significant hydrophilic property, plasma polymerization with ordinary alcohols, aldehydes, and esters did not produce hydrophilic films, as was expected. Fragmentations of the monomers at the oxygen atom sites were thought to be the reason. Therefore, nitrogen-containing monomers such as pyridine de-

rivatives and unsaturated amines have been employed to produce hydrophilic polymer films.<sup>3,4</sup>

Incidentally, we have recently found that propargyl alcohol (2-propyn-1-ol, PA) conducted plasma polymerization under very low electric power by which fragmentation of the monomer could be minimized. Abundant oxygen atoms, thus, survived in the resultant polymer yielded high wettability.<sup>5-7</sup> In addition, deposition rate of the polymer was considerably fast and the polymer film exhibited high transparency.

This article reports extensive study for preparation of hydrophilic plasma-polymers employing various oxygen-containing organic monomers for the purpose of explaining interrelation among chemical structures of the monomers, power consumption for sustaining the plasma polymerization, and wettability of the resultant polymers. Liquid monomers with different chemical structures involving hydroxyl, carboxyl, carbonyl, and etheric groups were employed for comparison. Measurement of water-contact angles on the polymer films and x-ray photoelectron spectroscopy (XPS) were both incorpo-

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rated with physico-chemical interpretation of the film characters.

## EXPERIMENTAL

### Materials

The oxygen-containing organic monomers employed for this experiment are listed in Table I. Monomers indicated with abbreviations of PA, PC, AA, AC, FA, EG, and EM were supplied from Nacalai Tesque Inc., Kyoto, and others were from Tokyo Kasei Kogyo Inc., Tokyo. All monomers were graded as guaranteed or extrapure reagents.

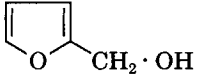
Glass slides for optical microscopy and poly(vinylidene chloride) film for food-wrapping were employed as solid substrates for polymer deposition, depending upon the purpose of researches, such as measurement of deposition rates, evaluation of wettability, and XPS interpretation, although the food-wrapping film involved certain derivative of fatty acid and epoxy vegetable oil as plasticizers within the polymer matrix.

### Plasma Reactor System

A plasma reactor system composed for the research is illustrated in Figure 1. The plasma chamber made of Pyrex glass had a diameter of 8 cm and a length of 20 cm, while its open end could be closed by a plastic disk with an aid of O-ring for air tightness. Two electric wires were mounted through the plastic disk. The chamber was evacuated with a rotary pump (300 L/min, Edwards Inc., High Vacuum Pump E2M-12, England) via a throttle valve and a cold trap. A three-way stopcock was installed in the downstream line to connect with either a McLeod vacuum gauge or air release.

The plasma chamber was internally installed with a pair of parallel electrodes, which was also parallel to the gas flow. The electrodes were made of aluminum, having a thickness of 1.5 mm and an area of  $100 \times 55 \text{ mm}^2$ , and were supported with four ceramic insulators having a 40 mm gap. Radiofrequency (RF) electric power of 13.56 MHz was supplied from a generator to the electrodes via a power meter (Samco International Lab. Inc., Model PM-43, Kyoto) and a matching network. A manifold with two needle valves was installed in the upstream line of the reactor to deliver either monomer gas or air.

**Table I Chemical Structures of Oxygen-Containing Monomers with Respective Abbreviations**

Monomer	Abbr.	Chem. Structure
Propargyl alcohol (2-propyn-1-ol)	PA	$\text{CH}\equiv\text{C}-\text{CH}_2\cdot\text{OH}$
Propargyl acid (2-propynoic acid)	PC	$\text{CH}\equiv\text{C}-\text{COOH}$
Methylbutynol (2-methyl-3-butyn-2-ol)	MBO	$\text{CH}\equiv\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\cdot\text{OH}$
Allyl alcohol (2-propen-1-ol)	AA	$\text{CH}_2=\text{CH}-\text{CH}_2\cdot\text{OH}$
Acrylic acid (2-propenoic acid)	AC	$\text{CH}_2=\text{CH}-\text{COOH}$
Acrylic aldehyde (2-propenal)	AD	$\text{CH}_2=\text{CH}-\text{CHO}$
Furfuryl alcohol (2-hydroxymethylfuran)	FA	
Ethylene glycol (1, 2-ethanediol)	EG	$\text{HO}\cdot\text{CH}_2-\text{CH}_2\cdot\text{OH}$
Ethylene glycol, dimethylether (1, 2-dimethoxyethane)	EM	$\text{CH}_3\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$

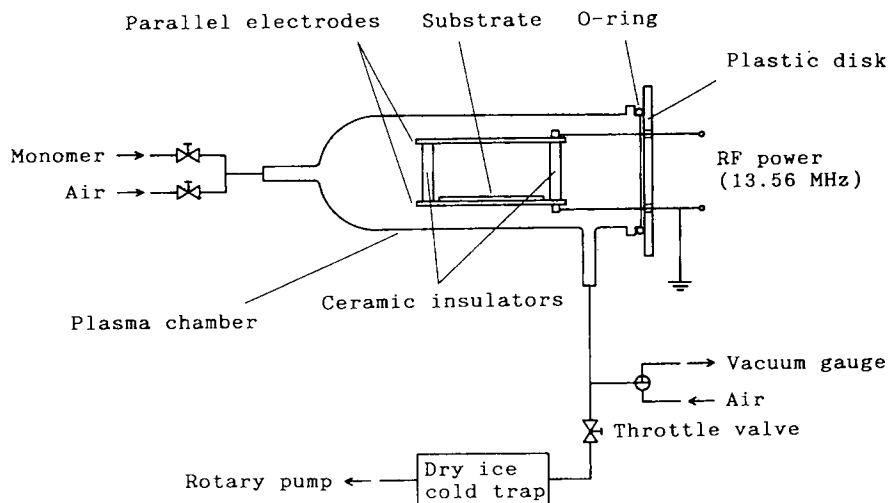


Figure 1 Schematic diagram of plasma reactor.

Any monomer gas was supplied from a small glass reservoir by continuous vaporization of the monomer liquid. The air line was opened when air plasma under RF discharge was used to clean up the interior of the plasma chamber before repeated plasma polymerizations.

### Preparation of Plasma-Polymer Films

The glass slides ( $76 \times 26 \text{ mm}^2$ ) and the wrapping film were dipped in ethanol for cleaning in advance. The wrapping film was cut into thin tapes ( $105 \times 3 \text{ mm}^2$ ), and every tape was tightly attached to one of the glass slide along the center line while the tape ends were wound to the rear side. A weak tension was applied to the tape during the process. The glass slide with the wrapping film was placed at the central position on the lower electrode.

The plasma reactor was evacuated down to approximately 0.03 Torr, while the stopcocks at the inlet position were closed. The stopcock on the monomer line was then partly opened so as to introduce monomer gases into the plasma reactor. The gas pressure was held normally at around 0.1 Torr, although some monomer liquids supplied lower gas pressure due to the high boiling points. After the pressure in the reactor reached equilibrium, the plasma excitation was initiated and sustained under control of the RF power by which hydrophilic polymer films were favorably produced on the substrates. The whole procedure was carried out at a room temperature of approximately  $23^\circ\text{C}$ . Polymers formed on the glass slides were subjected to measurement of the water-contact angles on the polymer surfaces, while sharp steps formed by peeling off of the wrapping film were used to measure the film thickness

of the plasma-polymer. The plasma-polymers deposited on the wrapping film were later subjected to the XPS research.

### Polymer Deposition Rates

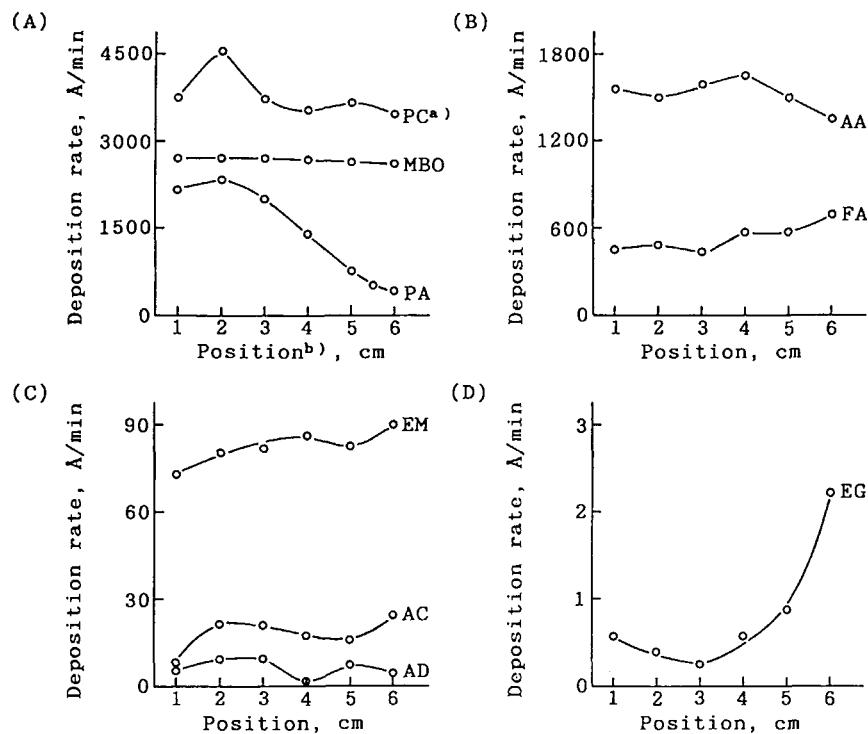
Deposition rates of the plasma-polymers were obtained by measuring film thicknesses formed during a unit of time. A Surface Profile Measuring System Dektak 3030 (Japan Vacuum Engineering Inc., Kanagawa, Japan) was employed for this measurement in that a fine needle moved for tracing a microstep made by removal of the wrapping film as mentioned above. Average roughness and steric profiles of the polymer surfaces were concurrently observed by this apparatus, and that information was helpful to qualify the polymer films obtained.

### Contact Angles of Water

The glass slide on which the plasma-polymer was deposited was laid horizontally, and  $10 \mu\text{L}$  of water was dropped onto the polymer using a microsyringe supported vertically by a stiff post. The advancing contact angle was quickly measured with a protractor while the drop was horizontally observed by a magnification lens.

### XPS Spectra

The thin tapes of the wrapping film on which the plasma-polymers were deposited were cut into pieces  $3 \times 3 \text{ mm}^2$  at appropriate points. A Shimadzu ESCA-750 Spectrometer incorporated with a ESPAC-100HIR Data Processing System (Shimadzu Inc.,



**Figure 2** Profiles of deposition rates of plasma-polymers derived from various monomers. (a) Measured after wiping off faint polymer dust covered on the sample film. (Polymer dust still remained inside.) (b) Distance from the upstream end of the glass slide.

Kyoto) was used to obtain XPS information from the sample pieces.

Relative ratios of atom numbers between oxygen and carbon (O/C) were calculated from peak areas of XPS spectra. Wave separation of  $C_{1s}$  spectrum was carried out using the curve-fitting method. At first, several peaks were considered from the hypothetical chemical structures of the polymers, and those peak positions, i.e., the binding energies, were determined from a table of XPS chemical shifts.<sup>8</sup> The peak width at half height of every peak could also be assumed referring to the same table. All the peak areas were integrated by controlling the peak heights so as to closely overlap with the given XPS spectra. Such data processing helped to avoid equivocal and subjective interpretation of the XPS spectra.

## RESULTS AND DISCUSSION

### Film Formation with Plasma-Polymers

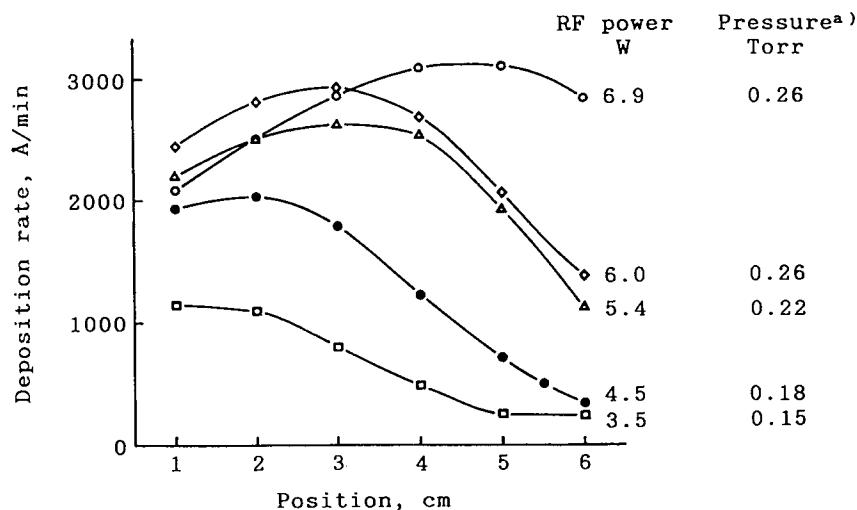
#### Profile of Deposition Rates on Substrates

The plasma reactor with a pair of parallel electrodes through which the monomer gases flow in a parallel direction is not favorable to obtain uniform film

thickness of the plasma polymer if the substrate has a fairly wide area. However, such an arrangement may be advantageous to know profiles of deposition rates along the gas flow in the discharge region that will be suggestive to determine the necessary residence time for efficient polymer deposition. A comparative study of the profiles obtained from various monomers may provide helpful clues to explore interrelations between the deposition rates of the polymers and chemical structures of the monomers.

Figure 2 shows the profiles of deposition rates derived from various monomers under the softest plasma conditions by which solid polymer film could be formed. It seemed that the profiles of deposition rates significantly varied due to different types of the chemical structures of the monomers.

In the case of a PC monomer, polymerization started immediately after the discharge was initiated, developing faint polymer dust on the substrate, and soon a thick layer of the polymer dust was formed. In order to have a solid film, the electric power should be reduced from the initial 15 W to 1.5 W, although some fine particles still fell down onto the solid film. It was supposed, therefore, that the film grew up thicker, including considerable amounts of the polymer dust. The fact was evidenced by a cloudy polymer film and significant roughness



**Figure 3** Profiles of deposition rates of PPPA under varying RF power. (a) Under discharge. Mass flow rate: 30 mg/min.

indicated by the surface profile measuring system. Samples subjected to the water-contact angle measurement and XPS interpretation were, therefore, preliminarily wiped to remove the polymer dust from the surface. FA conducted the polymerization, apparently yielding solid film, but faint polymer dust was deposited on the inner wall of the plasma chamber, suggesting that some polymer dust was included within the polymer film. Faintly clouded polymer film and roughness of the surface were the evidence.

The profiles of the deposition rates along the gas flow were classified into three types as follows: the first one was that the rates decreased simply towards the downstream direction; the second one was that the rates exhibited certain maxima within the position ranging 1–6 cm; and the third one was that the rates increased towards the downstream end of the substrates. Although some of the monomers indicated hybridized characters, rough sorting could be made with PA, PC, and MBO as the first group, AA, AC, and AD as the second, and FA, EG, and EM as the third. As a result of such grouping, monomers containing the triple bond in the chemical structure seemed to produce an abundance of active species for polymerization immediately after the monomers entered to the discharge region, and the number of active species gradually decreased towards the downstream direction due to consumption of the monomer materials. Monomers containing an olefinic double bond likely produced active species at a somewhat later time after the monomers entered to the discharge region. Other monomers, involving the cycloolefine ring and saturated bonds, probably needed longer residence time to produce active species so that the deposition rates went up towards

the downstream direction. The results implied that monomers having a triple bond generally carry out plasma polymerization more intensely than other types of chemical structures.

#### RF Power

In preparation of plasma-polymerized PA (PPPA), fine control of RF power supply was possible and the varied RF power also altered certain physico-chemical properties of the resultant polymers. Figure 3 shows the profiles of deposition rates of the PPPA at varying RF power. The maximum points of the deposition rates were found when the RF power was raised more than 5 W and the points shifted towards the downstream direction at a higher wattage. Although the profile of deposition rates of PPPA belonged to the first type as mentioned above when the polymerization was carried out with RF power below 5 W, high RF power such as 6.9 W resulted in the profile of the second or third type. It was considered, therefore, that high RF power activated certain sites of the monomer molecule other than the triple bond, so that longer residence time would have been required. Simply said, activation of the triple bond conducted the polymerization at the 1–3 cm region, and the activation of other sites did at the following range. Slightly higher inner pressures were measured when the RF power was increased, thus explaining that more intense fragmentation of the monomer took place within the discharge region.

It was especially interesting to know the interrelation between the RF power and the resultant polymers with respect to the physico-chemical properties. Figure 4 shows the contact angles of wa-

ter on PPPA produced by different RF power. Each curve exhibited much complication along the gas flow, but the general view informed the hydrophilic property of the polymers. No data was obtained at the position of 6 cm in the case of 3.5 W RF power because the polymer film was disintegrated by a drop of water.

In the range of RF power below 6.0 W, significant wettability was obtained and, in further detail, increase of RF power yielded higher water-resistibility of the polymer film. The latter quality would be due to higher crosslinking of the polymer network. In the case of higher RF power than 6 W, rather hydrophobic films were obtained. It was readily interpreted that some of the OH group was split off by the enhanced electron energy.

A subtle change of the quality along the gas flow was observed in the case of PPPA when the polymer was prepared with the RF power of 4.5 W. Although either polymer at any position was water resistant, the polymer at the 1–5 cm position became cloudy after contact with water and subsequent drying up. Such cloudiness seemed to be due to swelling by the water and/or dissolution of small molecules from the polymer matrix. It was also supposed that smaller molecules of the polymer were apt to be included in the film at upstream positions. PPPA, produced at positions of 5.5 and 6.0 cm, kept transparency after a fairly long immersion time in the water. It has been concluded that the hydrophilic PPPA film with a water-resistant property would be prepared on the substrate located at a somewhat downstream position of the discharge region under a selected plasma condition.

### **Operative Condition for Plasma Polymerization**

Selected operative conditions for polymerization of various monomers are listed in Table II. The data were obtained when the best hydrophilic films were prepared with the plasma reactor system employed in this study. The monomers were selected on the following bases: (1) boiling points were nearly 100°C or not very far from it; (2) the number of oxygen atoms in the monomer molecules were 1/3 those of carbon atoms or more if possible; (3) monomer molecules involved certain structural features, which would assist to preserve hydrophilic functions in the plasma-polymer. MBO was an exception from the basis (2), but the monomer was tested to know any shielding effect of OH group by adjacent two methyl groups against the plasma radiation.

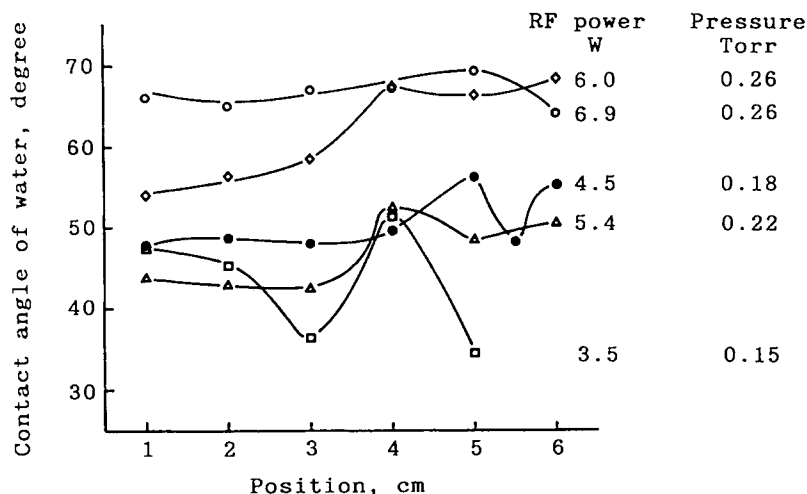
The RF power indicated in Table II are the values to sustain discharges of the monomer gases for preparation of solid polymer films. However, the

initiation of the discharge generally needed higher RF power than the values listed in this table. Therefore, loading of RF power should be manually controlled for initiation and then for steady-state operation. The experiment showed that alcohols and ethers needed narrower difference of RF power between initiation and steady-state operation than acids and aldehyde. Polymerization of AD under the ordinary plasma condition resulted in oily and sticky polymer film with an aldehyde smell. However, reduction of the mass flow rate and exceptionally low RF power made it to be a solid film. PA, MBO, and FA also produced somewhat sticky polymer films, but those were soon hardened after exposure to the ambient air at room temperature. Radicals left in the polymer films likely worked out for further crosslinking.

Inner pressures of the plasma reactor generally increased when the RF discharge of the monomers were applied.<sup>2</sup> This implies that intense fragmentations of the monomers or oligomers took place, while some of the fragments would be recombined later to form plasma-polymer films.

Because the operative conditions listed in Table II appear with random numerals, Figure 5 has been drawn for comparison of the necessary RF power for preparing solid polymer films. The figure was divided into two portions, (A) and (B), depending upon the scale of mass flow rates. The deposition rates of the polymers were indicated as four sizes of the marks. Straight lines bound between the marks and the origin represented characteristic slopes of the individual monomers, and a lower inclination of the slopes implied that the polymerization could be carried out with lower wattage of RF power at relatively high mass flow rates of the monomers. Broken lines drawn in the figure were to refer to the slopes that could not be terminated in (A) or (B).

In respect to the alcohol monomers, the slopes became steeper from PA to MBO, FA, AA, and EG in this order. In comparison of the acid monomers, PC showed an ordinary slope, while AC exhibited the steepest slope in all the monomers tested in this experiment. Roughly speaking, alcohols except for EG were polymerized at relatively low wattage of RF power, and the triple bond in the monomer molecules brought about a high rate of polymerization. In addition, alcohol monomers were smoothly vaporized from the reservoir compared with the homologous acid monomers, probably because of weaker intermolecular forces of the former than the latter. EG hardly yielded polymer film under relatively high RF power, whereas its dimethyletherized EM was polymerized at a much higher rate.



**Figure 4** Contact angles of water on PPPA produced under different RF power. Substrate: glass, drop volume: 10  $\mu\text{L}$ .

## Wettability of the Plasma-Polymers

### Oxygen Content

The plasma-polymers derived from the oxygen-containing monomers were evaluated in respect to wettability by measuring contact angles of water on the polymer films. Because the oxygen content of the polymer was undoubtedly an important factor for developing wettability, O/C atom ratios of the monomers and polymers were compared and listed in Table III. The data of the monomers were cal-

culated from the molecular formulae, while those of the polymers were from the peak areas of XPS spectra. Care had been taken to find no  $\text{Cl}_{2p}$  signal in the XPS spectra because the wrapping film employed as the substrate was poly(vinylidene chloride).

Polymer films derived from AC, AD, and EG dissolved remaining dispersed fragments when water drops were placed on the polymers for measurement of the contact angles of water. It has been supposed that these polymers did not grow to be large and

**Table II** Operative Conditions for Plasma Polymerization of Oxygen-Containing Monomers

Monomer	Boiling Point ( $^{\circ}\text{C}$ ) <sup>a</sup>	RF Power (W)	Operative Condition		Mass Flow Rate <sup>b</sup> (mg/min)	Deposition Rate ( $\text{\AA}/\text{min}$ )
			Pressure (Torr)			
			Before Discharge	During Discharge		
PA	114	4.5	0.06	0.18	28.4	500
PC	144 <sup>c</sup>	15.0	0.04	0.10	12.8	3570 <sup>d</sup>
MBO	104 <sup>e</sup>	30.0	0.13	0.35	62.2	2670
AA	97	40.0	0.21	0.36	24.4	1470
AC	141	18.0–19.0	0.03	0.08	0.2	50 <sup>f</sup>
AD	52	1.3–2.5	0.03	0.05	0.4	10
FA	170	2.0	0.01	0.07	3.5	740 <sup>g</sup>
EG	198 <sup>h</sup>	12.0–13.0	0.03	0.08	0.3	3
EM	83–84	38.0–41.0	0.15	0.35	21.1	90

<sup>a</sup> Literature value.

<sup>b</sup> Calculated by weight decrease of monomer reservoir for measured time.

<sup>c</sup> Decomposition (bp 57 $^{\circ}\text{C}$  at 12 Torr).

<sup>d</sup> Measured after wiping off faint polymer dust covered on the sample film.

<sup>e</sup> 60 $^{\circ}\text{C}$  at 120 Torr.

<sup>f</sup> The film surface was rough.

<sup>g</sup> Probably involved faint polymer dust.

<sup>h</sup> 195–198 $^{\circ}\text{C}$  appeared in another literature.

crosslinked molecules. The contact angles measured and listed in Table III roughly coincided with the order of inclination of the lines drawn in Figure 5, and PPPA indicated the highest wettability.

High wettability was substantially due to an abundance of oxygen atoms in the resultant polymers so that the soft plasma conditions under low RF power was advantageous. In comparison to O/C data in Table III, the resultant polymers did not show much difference in O/C values in spite of significant variation of the contact angles of the water. It was supposed, therefore, that the O/C data were measured by the XPS spectra informing average values from the utmost surface to approximately a 50 Å depth. It should be considered that the contact angles have closer relation to the utmost surface of the polymer films.

### Spatial Arrangement of Oxygen Atoms

The  $C_{1s}$  peaks obtained by the XPS were subjected to the peak separation process assuming six possible atom groups in the polymer molecules. Table IV shows the names of the atom groups with peak numbers and the related data. The curve-fitting method by integration of those peaks was employed, changing the peak height of every peak. The results are listed in the same table with the individual peak areas.

The presence of oxygen atoms in the polymer molecules were characterized in three different ways, as indicated in Table V. The O—C/C—C ratio repre-

**Table III** Film Characters of Plasma-Polymers Derived from Oxygen-Containing Monomers

Monomer	Contact Angle of Water (Degree) <sup>a</sup>	O/C <sup>b</sup>	
		Monomer	Polymer <sup>c</sup>
PA	48	0.33	0.34
PC	52 <sup>d</sup>	0.67	0.34 <sup>d</sup>
MBO	65	0.20	0.25
AA	80	0.33	0.29
AC	dissolved	0.67	0.36
AD	dissolved	0.33	0.36
FA	66	0.40	0.34
EG	dissolved	1.00	0.34
EM	76	0.50	0.30

<sup>a</sup> Substrate: glass, drop volume: 10  $\mu$ L.

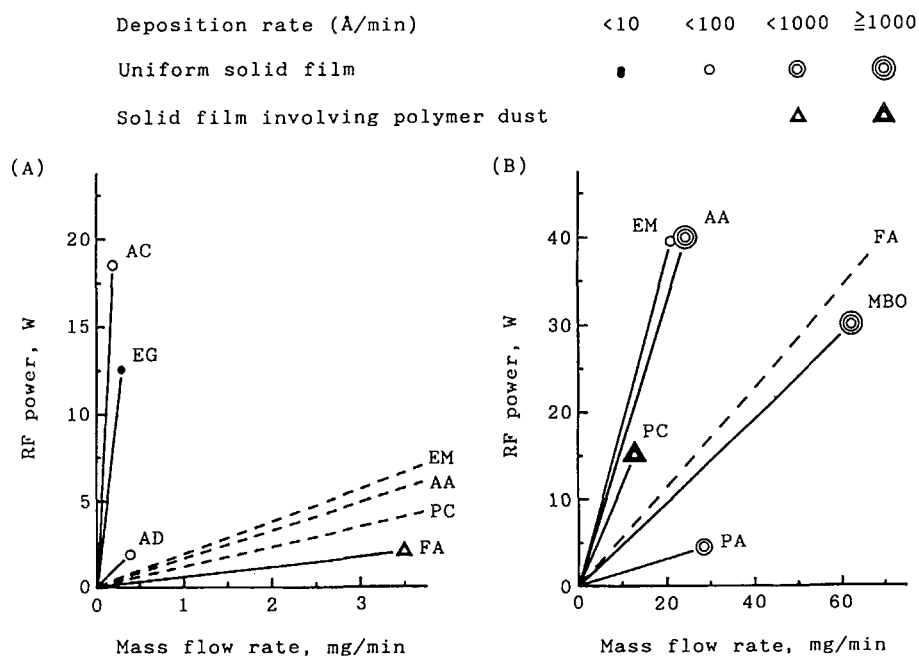
<sup>b</sup> Ratio of atom numbers.

<sup>c</sup> Calculated from peak areas of XPS spectra.

<sup>d</sup> Measured after wiping off faint polymer dust covered on the sample film.

sented a parameter for distribution of oxygen atoms in the carbon chains. Location of oxygen atoms evaluated as the ratios of side chain/principal chain could imply the probability that the oxygen atoms existed more at the surface of the polymer matrix. Hydroxyl and carboxyl functions are the representative hydrophilic groups so that the ratios of these groups to total oxygen groups may also enhance the wettability.

Combining the data of Tables III to V, it can be said as follows: PA, PC, and FA produced polymers



**Figure 5** RF power needed for plasma polymerization of various oxygen-containing monomers.



**Table IV Separation of C<sub>1s</sub> Spectra into Peaks of Representative Atom Groups by Curve-Fitting Method**

Peak No. Atom group	1 Carbon C—C—C	2 Alcohol C—OH	3 Ether C—O—C	4 Ketone/Aldehyde $\begin{array}{c} R_1 \\ \diagdown \\ C=O \\ \diagup \\ R_2 \end{array}$	5 Carboxyl $\begin{array}{c} -C-OH \\    \\ O \end{array}$	6 Carbonate $\begin{array}{c} -C-O-R-O- \\    \\ O \end{array}$
Binding energy (eV)	284.60	286.40	287.10	287.60	288.60	290.30
Peak width at half height (eV)	1.00	0.80	1.80	1.00	1.20	2.60
Composition of Peak Area (%)						
Monomer						
PA	4.8		8.0	62.8	3.9	8.4
PC	7.1		16.8	54.7	0.2	4.2
MBO	6.5		11.9	67.0	0.2	5.3
AA	4.5		15.9	65.5	0.2	5.4
FA	3.9		4.5	59.4	3.3	10.0

having almost the same O/C content but the O—C/C—C value of PC was significantly low. However, values of the side chain/principal chain and the hydrophilic groups/total oxygen groups of PC were higher than others. The PC monomer itself is rather chemically unstable and was polymerized with polymer dust falling on the film surface. It has been supposed that the oxygen atoms in the PC monomer was intensely split off under the plasma discharge, but the remaining oxygen atoms were still located in the side chain. On the other side, the polymer derived from FA retained large number of oxygen atoms in the molecules but the oxygen atoms were rather located at the principal chain to build up the polymer matrix. A low value of hydrophilic groups/total oxygen groups was indicated as the evidence.

Comparison between the polymers derived from MBO and AA were also interesting. Although MBO has a lower oxygen content than the other monomers, the hydroxyl group was well protected and preserved by the adjacent two methyl groups during the plasma polymerization. Regarding AA, the hydroxyl group was significantly left in the polymer; however, the dense hydroxyl group at the polymer surface often turn its orientation towards the inside, thus, less wettable surface than anticipated would be obtained.<sup>9-11</sup> Comparison of contact angles on MBO and AA polymers indicated a much higher value for AA than MBO polymers.

#### Degree of Unsaturation

In addition to the data obtained from XPS, the degree of unsaturation was calculated from the element

**Table V Classification of Oxygen Atoms as Forms of Presence in Hydrophilic Plasma-Polymers**

Monomer	O Atoms Bound with C Atoms O—C/C—C <sup>a</sup>	Location of O Atoms Side Chain/ Principal Chain <sup>b</sup>	Hydrophilic Groups/ Total Oxygen Groups <sup>c</sup>
PA	19.86	0.27	0.17
PC <sup>d</sup>	13.05	0.29	0.23
MBO	14.43	0.23	0.18
AA	21.22	0.29	0.22
FA	24.70	0.23	0.15

<sup>a</sup> Calculated from peak areas of XPS spectra by using equation: O—C/C—C = (2 + 3 + 4 + 5 + 6)/(1); Peak numbers are listed in Table IV.

<sup>b</sup> (2 + 4 + 5)/(3 + 6).

<sup>c</sup> (2 + 5)/(2 + 3 + 4 + 5 + 6)

<sup>d</sup> Measured after wiping off faint polymer dust covered on the sample film.

**Table VI Degree of Unsaturation of Oxygen-Containing Plasma-Polymers**

Monomer	Elemental Analysis of Polymers (%)			Ratio of Atom Numbers			Degree of Unsaturation <sup>b</sup>
				Elemental Analysis		XPS <sup>a</sup>	
	C	H	O	O/C	O/C		
PA	66.13	7.30	26.57	0.34	0.30	1.32	2.88
MBO	76.98	9.52	13.50	0.25	0.13	1.47	2.69
AA	69.39	9.83	20.66	0.29	0.22	1.69	1.90

<sup>a</sup> Calculated from peak areas of XPS spectra.

<sup>b</sup> Degree of unsaturation for  $C_wH_xN_yO_z$ :  $R = w + 1 + (y - x)/2$ .

composition.<sup>5</sup> Table VI shows the results for three polymers. It should be noted that the ratios of atom numbers were somewhat different from the XPS data to the elemental analysis, but the calculation of the degree of unsaturation needed an H/C atom ratio from the elemental analysis. The polymer derived from AA indicated the lowest value. Because the lower degree of unsaturation decreases the critical surface tension of the polymer, the AA polymer was less wettable than other polymers.

## CONCLUSION

All the results obtained in this experiment has led to the conclusion as follows: alcohols having triple bonds were the most profitable monomers among the oxygen-containing compounds for preparation of hydrophilic polymer films by the plasma polymerization technique. Those were readily polymerized, forming transparent films on any solid substrates. The triple bonds conducted plasma polymerization under low wattage of RF power so that oxygen atoms could be preserved in the resultant polymers in the forms of oxygen-containing functional groups. At present, PA was the most promising monomer in this respect. In the case of using a water-containing PA as a monomer, the wettability could be further enhanced.<sup>5,6</sup> Finally, it may be said that monomers should be selected by two points of view: one is "polymerization site" and the other is "functional site." The former is to conduct poly-

merization with the least damage of the latter, and the latter is advised to be independent from the former, although some complicated interrelation between the two sites will not be avoided.

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