

Structural Interpretation of Plasma-Polymerized Propargyl Alcohol

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Synopsis

Vapor of propargyl alcohol under reduced pressure was glow-discharged for plasma polymerization by which hydrophilic polymer film could be deposited onto a solid substrate. The hydrophilic property was more enhanced with use of the same monomer containing water. An interpretation of chemical structures of the polymer molecules was therefore attempted to discover the reason of the hydrophilic property. The polymer materials were subjected to IR spectroscopy, ^{13}C -NMR and ^1H -NMR spectroscopies, elemental analysis, number average molecular weight determination, mass spectrometry, and other wet chemical analysis for $\text{C}=\text{O}$ and $\text{C}=\text{C}$. The IR spectra of the polymers showed the presence of OH, $\text{C}=\text{O}$, and $\text{C}=\text{C}$ groups with a disappearance of $\text{C}\equiv\text{C}$ group of the monomer. It was also found that the molecular formula of a solvent extract of the polymer derived from the plain monomer was $\text{C}_{26}\text{H}_{36}\text{O}_9$, 490, involving four hydroxyl, one carbonyl, and two to three olefinic unsaturation groups within a unit molecule. On the other hand, the polymer from 60% water-containing monomer showed its molecular formula as $\text{C}_{44}\text{H}_{66}\text{O}_{18}$, 890, containing seven to eight hydroxyl, two carbonyl, and one to two olefinic unsaturation groups. This information was used to establish the symbolic chemical structures of the polymer molecules. It has been found that both polymers were not as much crosslinked as other plasma polymers because of having side chains with fewer branching. The oxygen atoms were retained in the polymer not only as the forms of OH and $\text{C}=\text{O}$ but also as a member of the principal frame of the polymers.

INTRODUCTION

Techniques of plasma polymerization have been currently employed for deposition of polymer thin films on solid substrates which were located within a glow discharge region of various monomer gases under a reduced pressure.¹⁻³ Monomers having different characters yielded variety of physical and chemical properties of polymers, namely, hydrophobic or hydrophilic nature, light transmittance, adherence, material permeability, and dielectric characteristics. Whereas oxygen-containing plasma polymers have been awaited for preparing hydrophilic coating films using monomers such as alcohols and carboxylic acids, the attempt was hardly successful because an efficient fragmentation of oxygen-containing primitive materials took place during the plasma polymerization process. It followed, therefore, that the resulting polymers were not as satisfactorily hydrophilic as had been expected. However, 2-propyn-1-ol (propargyl alcohol, PA), the simplest aliphatic alcohol having triple bond, has been recently found to be polymerized under very low electric power with the minimum elimination of oxygen atoms.⁴ The report also described that the oxygen content of the polymer was further increased when the plasma polymerization was carried out with the same monomer containing

water (PW); hence it made the polymer film more hydrophilic. Change of the water concentration in the monomer from 0 to 80% resulted in increasing the oxygen content of the polymer from 25 to 40%, while the contact angle with a water drop on the plasma-coated glass plate decreased from 45° to 18°. The same text involved other data of the polymer such as deposition rate, IR spectrum, solubility in different solvents, thermal properties, element composition, and average molecular weight. This article reports an interpretation of chemical structures of the plasma-polymerized propargyl alcohol (PPPA) and the related plasma polymer derived from 60% water-containing propargyl alcohol (PPPW). Their chemical structures were depicted by integrating the results obtained from the above experiments, together with some additional information such as ^{13}C -NMR and ^1H -NMR spectroscopies, mass spectrometry, and quantitative analysis of $-\text{OH}$, $\text{C}=\text{O}$, and $\text{C}=\text{C}$. The proposed chemical structures are symbolic illustrations at number average molecular weights being composed of various partial structures, but still they will be helpful to understand the specific characters of the polymers.

EXPERIMENTAL

Monomer

PA was an extra pure reagent supplied from Nakarai Chemicals Ltd. (Kyoto) and was used without further purification. Since it was known that the water-containing PA supplied vapor of practically the same composition as the liquid phase under the reduced pressure,⁴ 60% water-containing PA (PW) was prepared as a monomer to produce PPPW. The monomers were stored in a small glass reservoir to connect with an inlet pipe line of a plasma reactor. Shielding outside of the reservoir from light by an aluminum foil was desirable to prevent coloring of the monomers.

Plasma Reactor System

A schematic diagram of the plasma reactor system (Samco International Lab., Kyoto) is illustrated in Figure 1. A glass bell jar having a diameter of 25 cm and a height of 30 cm was put on a stainless steel base using a rubber gasket for airtightness. The reactor was evacuated from the bottom by a rotary pump (300 l/min) via a dry ice-ethanol cold trap. A gas pressure in the reactor system was monitored by a thermocouple vacuum gauge. The parallel electrodes consisted of a drum-shaped upper electrode and a tablelike lower electrode both having a diameter of 10 cm. The upper electrode was drilled to open 12 nozzles at the lower side and was fixed to have an electrode gap of 5 cm. The monomer gas evaporating in the reservoir was transported into the upper electrode via a stopcock and was diffused downward from the nozzles onto the lower electrode. High-frequency electric power of 13.56 MHz was supplied from a generator to the parallel electrodes via a power meter and a matching network.

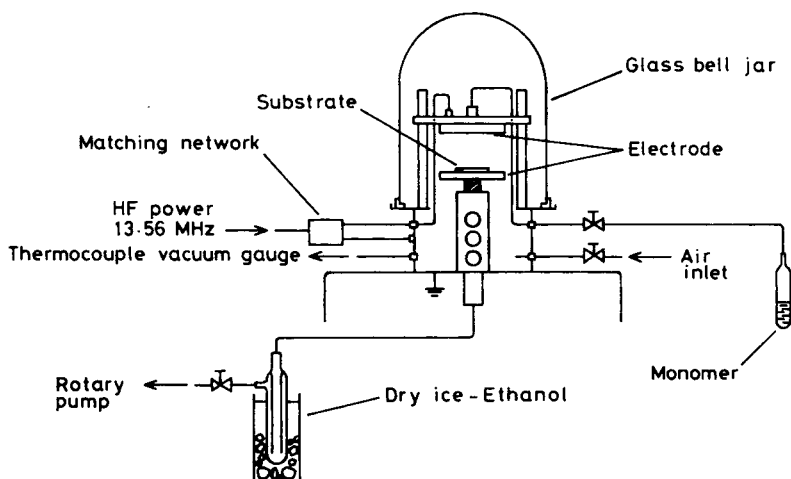


Fig. 1. Schematic diagram of plasma reactor system.

Procedure of Plasma Polymerization

A glass plate having a diameter of 10 cm was put on the lower electrode, and the plasma apparatus was evacuated down to about 0.01 Torr while the stopcock of the monomer reservoir was closed. PA or PW was then supplied to the reactor by opening the stopcock until the pressure was equilibrated at approximately 0.1 Torr. The plasma excitation was initiated and sustained by controlling the high-frequency electric power. The polymer film was deposited on the glass plate at an electric power of 5 W. The gas pressure was raised to 0.6 Torr during the plasma process because various types of fragmentations took place rather than the polymerization.

Preparation of Sample for Analyses

Since PPPA and PPPW were most soluble in methanol among conventional organic solvents,⁴ the plasma polymers produced on the glass plates were scraped off and dissolved in methanol with stirring. The suspensions were centrifuged at 3500 rpm for 15 min, and the supernatants were decanted to get methanol solutions of the polymers. The residues were again extracted in the same manner. The combined methanol extracts of the individual polymers were evaporated, and the residual polymers were dried *in vacuo* and powdered.

Spectroscopies

IR spectra were recorded on a Shimadzu Model IR-400 using KBr disk method for the powdered polymers and liquid film method for the monomer. ¹³C-NMR spectra were obtained using a Varian Model CFT-20 (20 MHz) and a Varian Model XL-300 (75 MHz). ¹H-NMR spectra were measured with a Japan Electron Optics Model JNM-PM60SI (60 MHz) and a Varian Model XL-300 (300 MHz). The measurements were run using tetramethylsilane as an internal standard and CD₃OD as a solvent.

Mass spectra were obtained employing Hitachi Model M-80, which was in operation as a secondary ion mass spectrometry (SIMS) with samples in glycerine spread on a silver plate.

Molecular Weight Determination

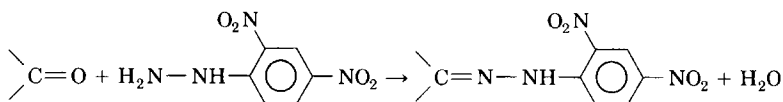
Number average molecular weight was measured by Knauer Dampfdruck Osmometer at 45°C using methanol-tetrahydrofuran (1:4) as a solvent and benzil ($C_{14}H_{10}O_2 = 210.22$) as a standard material. Thermistor responses against the standard solutions of known molar concentrations were plotted to establish a calibration curve by which number average molecular weights of the sample polymers were calculated.

Determination of Hydroxyl Group

A 125 μ L of chloroform was added to five to six drops of tetramethylsilane and diluted to 5 mL with CD_3OD medium. A part of the solution was used for a blank test in order to determine signal intensities of protons remaining in the medium as impurities. The other part of the solution was saturated with PPPA or PPPW. The total signal intensities of protons of the sample solutions were measured and corrected by subtracting the intensities of chloroform and the blank value of the medium, the latter of which was proportional to the former. The number of the hydroxyl group within a unit molecule was calculated from a ratio of hydroxyl protons to all protons in the sample on the basis of the data of elemental analysis.

Determination of Carbonyl Group

A gravimetric method using 2,4-dinitrophenylhydrazine was employed for a determination of carbonyl group. A saturated solution of the reagent in equivolume mixture of methanol and 2M hydrochloric acid was prepared, and 20 mL of the reagent solution was mixed with 4 mL of methanol solution of 10 mg polymer sample. After standing for one night, hydrazone precipitated was collected on a micro glass filter, washed repeatedly with 2M hydrochloric acid and then distilled water, and dried *in vacuo*. Nitrogen content of the hydrazone was then determined by elemental analysis, and the percentage composition of carbonyl group was calculated by the following equations:^{5,6}



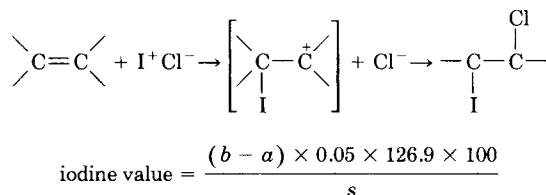
$$\text{>C=O} (\%) = \frac{N \times 0.4997}{A - N \times 3.215} \times 100$$

where A is the weight (mg) of hydrazone taken for nitrogen analysis and N is the nitrogen content (mg) in A (mg).

Determination of Olefinic Unsaturation

A 10 mg of the polymer sample was placed in an iodine flask and dissolved with 5 mL of methanol. A volume of 5.00 mL of Wijs' solution⁷ was added for

reaction and was shaken while a plug of the flask was closed. After standing for 2 h, 5 mL of 10% potassium iodide solution was introduced into the flask, and the reaction mixture was transferred into a beaker using 25 mL of methanol. The reaction mixture was immediately titrated potentiometrically with 0.05*N* sodium thiosulfate using a platinum tip as an indicating electrode. A blank test was run with the same method but without the sample. Content of the olefinic unsaturation was given as an iodine value which was calculated by the following equations^{6,8}:



where *a* is the volume of 0.05*N* Na₂S₂O₃ consumed for the titration of the sample (mL), *b* is the volume of 0.05*N* Na₂S₂O₃ for the blank test (mL), and *s* is the sample weight (mg).

RESULTS AND DISCUSSION

IR Spectrum

IR spectra of PPPA and PPPW exhibited strong resemblance to each other except that intensities of absorption bands at 3350 and 1715–1700 cm⁻¹ were slightly stronger in the spectrum of PPPW. Figure 2 shows the IR spectra of PA monomer and PPPA, and assignment of their absorption bands are listed in Table I. The spectrum of PPPA showed the presence of OH, C=O, and C=C groups with a disappearance of C≡C group of PA. These data

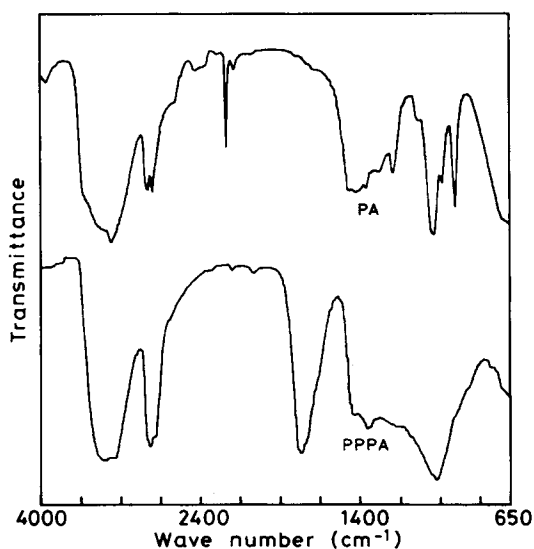


Fig. 2. IR spectra of PA and PPPA.

TABLE I
 Assignment of IR Absorption Bands of PA and PPPA

PA		PPPA	
Absorption band (cm ⁻¹)	Assignment	Absorption band (cm ⁻¹)	Assignment
3400	O—H stretch	3350	O—H stretch
3290	C—H stretch in alkyne	2900	C—H stretch
2930, 2880	C—H stretch	1700	C=O stretch
2140	—C≡CH stretch	1500–1300	O—H deformation
1500–1260	O—H deformation		CH ₃ deformation
1230, 1030, 920	C—O stretch		C=C stretch
650	C—H deformation	1200–900	—CH=CH ₂ deformation
			C—O stretch

implied: (1) the polymer propagated mainly consuming triple bonds of the monomer; (2) oxygen atoms of PA were preserved densely in PPPA compared with other oxygen-containing plasma polymers; (3) some of the OH group in the monomer were converted to C=O group that would be a result of electron impact in the glow discharge. The absorption band of C=O stretch was significantly wider than usual and shifted from the normal position to lower wave number. The wide absorption band indicated that the C=O group was surrounded by complicated chemical structures, and the shift to lower wave number suggested chemical interactions such as conjugation with C=C group and intramolecular hydrogen bond with —OH. The strong resemblance of IR spectra between PPPA and PPPW implied that the water vapor was dissociated in the plasma-producing OH radical, which was then associated with the polymer propagation as the similar mechanism as the OH group in PA.

NMR Spectrum

¹³C-NMR spectrum of PPPA is given in Figure 3, and the measurement was run with 20 MHz at number of repetitions above 60,000. No further detail was obtained with use of 75 MHz NMR. The polymer showed very broad spectra, as if its base line drifted. Such characteristic behavior was often seen in other plasma polymers suggesting that the polymer molecules included many irregular and complicated networks in their chemical structures. PPPW showed a similar spectrum as PPPA, but a small peak ranging $\delta = 124\text{--}140$ ppm having a center at $\delta = 129.37$ ppm was observed in the case of PPPA, by which relatively large number of aryl or olefinic groups were thought to be incorporated with the whole molecular structure compared with the case of PPPW. Either spectrum exhibited steep rise in the integral curve at the ranges of $\delta = 10\text{--}50$ ppm and $\delta = 55\text{--}90$ ppm before and after the solvent peak. The former range was assigned to alkanes or alicyclic group, and its signal intensity was the strongest in the spectrum, so that these groups seemed to be dominant in composition of the molecular structure. The latter range is an area where signals of alcohols appear overlapping with that of alkynes. However, the signal was assigned to various aliphatic carbons bound to

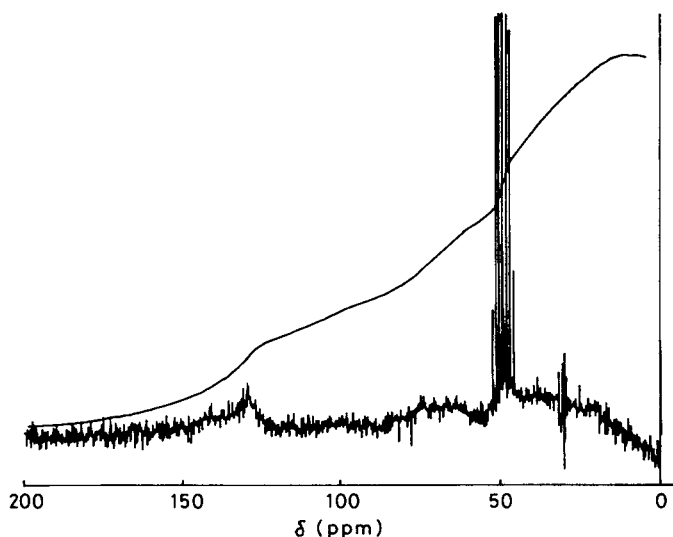


Fig. 3. ^{13}C -NMR spectrum of PPPA : CD_3OD medium.

hydroxyl group rather than to alkynes, because the absorption band of the triple bond in the IR spectrum of PA thoroughly disappeared in that of the polymer and the central position of the NMR signal was shifted to much higher magnetic field than that of common alkynes.

^1H -NMR spectra of PPPA and PPPW at 60 MHz were also broad as shown in Figures 4 and 5 and respective assignment of their signals are tabulated in Tables II and III. These assignments were also verified by high resolution NMR at 300 MHz. Hydroxyl proton in either PPPA or PPPW gave a sharp singlet spectrum overlapping with a signal of residual protons of the solvent. The spectrum of PPPA showed some broad signals of aryls and many alkyls.

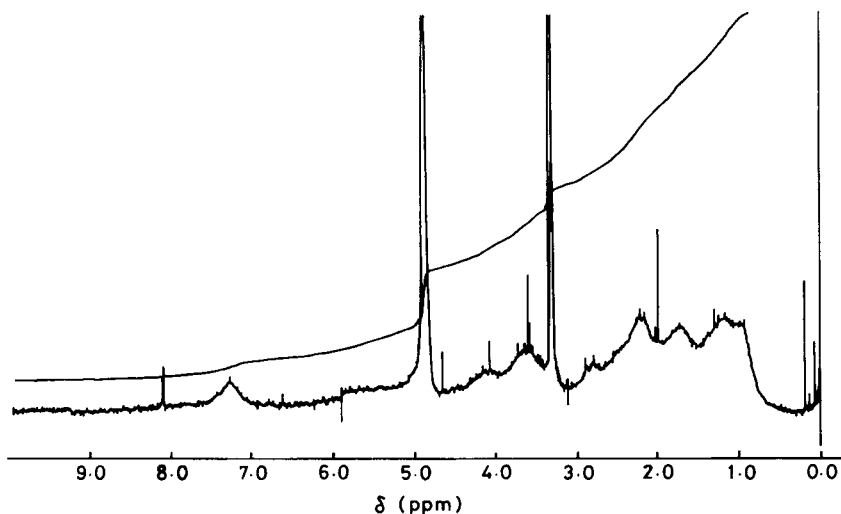
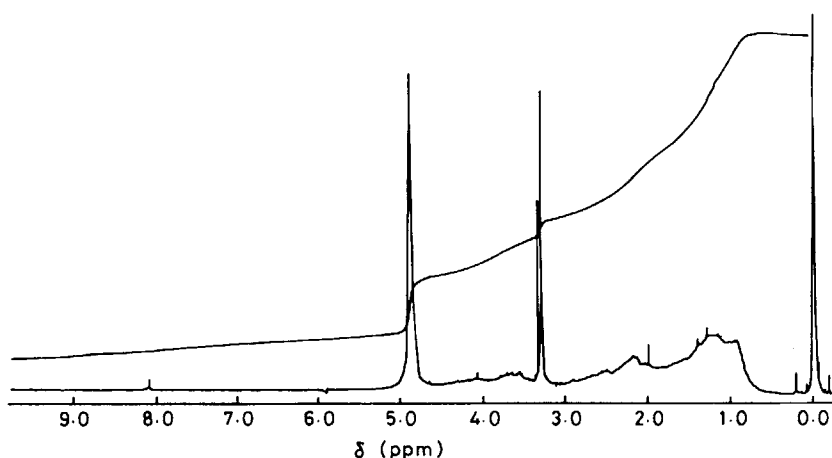


Fig. 4. ^1H -NMR spectrum of PPPA : CD_3OD medium.

Fig. 5. $^1\text{H-NMR}$ spectrum of PPPA : CD_3OD medium.TABLE II
Assignment of $^1\text{H-NMR}$ Spectrum of PPPA

δ (ppm)	Assignment
1.10-1.90	$\text{CH}_3\text{---C---Y}$ (Y: H, Ph, C=O)
1.20-1.30	$\text{R---CH}_2\text{---R}'$
1.65-1.75	$\text{CH}_3\text{---C=C---C=O}$
1.90-2.00	CH_3COR
1.95-2.05	$\text{CH}_3\text{---C=C---Y}$, CH_3COOY (Y: conjugated system)
2.20-2.50	$\text{CH}_3\text{---Ph}$
2.60-2.90	$\text{R---CH}_2\text{---Ph}$
3.65-3.75	$\text{CH}_3\text{---O---Ph}$
4.10-4.20	$\text{R}_2\text{CH---OH}$
4.80-4.90	OH
6.90-7.50	Ph-H, Ph-CH=C-

No evidence of the presence of aldehydes or free carboxyls was found in the IR and NMR spectra of PPPA and PPPW. The results of these spectroscopies were in agreement with the following theories related with radical reaction⁹: (1) a proton of aldehyde is very active to be readily split off; (2) the radical reaction hardly forms carboxyl because of the effect of electronegativity of the oxygen atom.

TABLE III
Assignment of $^1\text{H-NMR}$ Spectrum of PPPW

δ (ppm)	Assignment
0.90-1.00	$\text{CH}_3\text{---R}$
1.20-1.30	$\text{R---CH}_2\text{---R}'$
1.10-1.90	$\text{CH}_3\text{---C---Y}$ (Y: C=O, H)
1.95-2.05	$\text{CH}_3\text{---COR}$
1.95-2.10	$\text{CH}_3\text{---C=C---Y}$, CH_3COOY (Y: conjugated system)
4.80-4.95	OH

Average Molecular Weight

In order to determine number average molecular weight, methanol-tetrahydrofuran (1 : 4) solutions of PPPA and PPPW were subjected to vapor pressure osmometry. Although the polymers were most soluble in methanol, the methanol solution did not work with a proper sensitivity for the determination. The solvent mixture was therefore chosen for practical sensitivity and solubility of the polymers. Unfortunately, it was found that the solvent mixture did not show high solubility to PPPA in contrast to PPPW as listed in Table IV, so that the samples for the molecular weight determination were taken from the methanol-tetrahydrofuran extracts of the polymers. It may be clear that the average molecular weight of PPPA in the table was of a fraction of smaller molecular species, i.e., 63%, in the polymer. Percentage compositions of elements in either intact polymers or methanol-tetrahydrofuran extracts were also determined by microelemental analysis and listed in the same table.

As shown in Table IV, the molecular formula of PPPA was calculated to be $C_{26}H_{36}O_9$, $\bar{M}_n = 490$ and that of PPPW was $C_{44}H_{66}O_{18}$, $\bar{M}_n = 890$. The former molecular weight would be much lower than that of the intact PPPA, but the elemental compositions did not significantly differ from each other, so that the chemical structures of the intact PPPA and the methanol-tetrahydrofuran extract were thought to be strongly analogous. The latter molecular weight was practically the same as that of the intact PPPW because of the high solubility to the solvent mixture, but the value was still low in comparison with other known plasma polymers. One reason for the low molecular weight was interpreted by inclusion of small molecular species left unpolymerized under the low wattage of the plasma condition. The number average molecular weight measurable with the vapor pressure osmometry primarily indicates much lower value than a weight average molecular weight if the polymer possesses wide distribution to small molecular species. A simple calculation with regard to the oxygen content suggested that PPPW incorpo-

TABLE IV
Physical and Chemical Properties of PPPA and PPPW

	PPPA	PPPW
Intact polymer		
Element composition (%)		
H	7.30	7.44
C	66.13	59.08
O	26.57	33.48
Methanol-THF extract		
Fraction extracted (%)	63.0	99.9
Element composition (%)		
H	7.39	7.51
C	64.77	59.77
O	27.84	32.72
Average molecular weight	490	890
Molecular formula	$C_{26}H_{36}O_9$	$C_{44}H_{66}O_{18}$
Degree of unsaturation ^a	9	12

^a Degree of unsaturation for $C_wH_xN_yO_z$: $R = w + 1 + (y - x)/2$.

rated three oxygen atoms per unit molecule of the average molecular weight from outside of PA ($C_3H_4O = 56.06$). Degree of unsaturation was also calculated for PPPA and PPPW, resulting in 9 and 12, respectively. Considering the molecular weight of PPPA measured with the methanol-tetrahydrofuran extract, the intact PPPA would include unsaturated bonds more densely than PPPW. Their IR spectra implied that the unsaturated bonds were double bonds.

Mass Spectrum

Mass spectrometry has recently been employed as an absolute method for determination of molecular weight distribution of polymers. However, an attempt to obtain the same information of PPPA and PPPW was unsuccessful either by using electron ionization or field desorption. Secondary ion mass spectrometry with the polymer samples in glycerine matrix in the range of $m/z = 100-1500$ gave mass spectra as shown in Figure 6. The figure illustrates only dominant peaks, while blank signals from the glycerine matrix were eliminated.

The largest mass numbers appeared in the spectra at $m/z = 1462$ for PPPA and $m/z = 1496$ for PPPW, while very small mass numbers distributed around a range of $m/z = 100-200$. Either spectrum showed three characteristic regions. The first one was composed of $m/z = 365$ and 379 and the second one was of $m/z = 443, 457, 471, \text{ and } 485$. These mass numbers stepped up with a differential mass number of 14. The third one was of $m/z = 523, 567, 611, 655, 699, 743, 787, 831, \text{ and } 875$ with an increment of 44. The differential mass number of 14 seemed to be due to an increment of $-CH_2-$, while the differential mass number of 44 was possibly resulted from a replacement of $-H$ with $-C_2H_5O$, e.g., $-CH_2-CH_2-OH$. It must be mentioned that

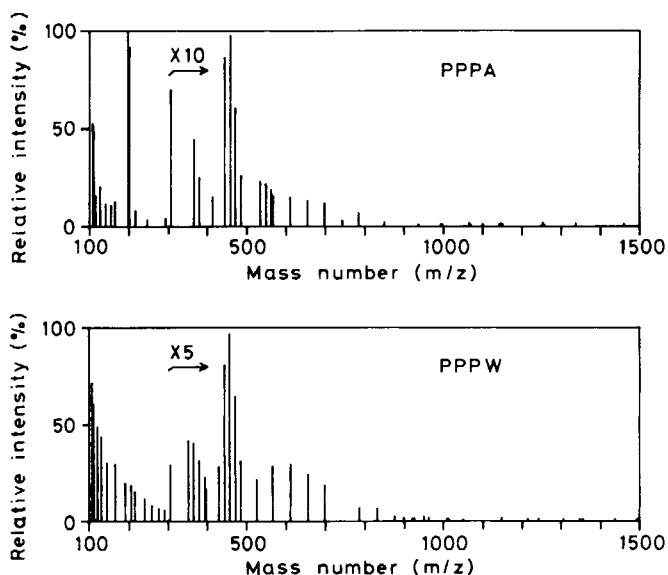


Fig. 6. Mass spectra of PPPA and PPPW.

the dominant signals mostly appeared at odd mass numbers. Considering the valency of the carbon atom, the surrounding four atom groups such as alkyl, OH, and H have odd mass numbers; therefore, molecules with carbon skeleton are mostly of even mass numbers. The above frequent appearance of odd mass numbers implied that the polymers underwent efficient fragmentations as a result of primary ion impact. The intact polymers were thought to have somewhat higher molecular weights than those obtained in the mass spectra.

Determination of Functional Groups

Hydroxyl group is the most important functional group participating in the hydrophilic property. Acetylation is a conventional means for determination of the group, but this method was not usable for PPPA and PPPW, since only methanol was an effective solvent for the polymers. Therefore, $^1\text{H-NMR}$ spectroscopy was employed to determine the hydroxyl group, because the group exhibited a sharp singlet signal independently in the spectrum. The composition ratios of the hydroxyl protons to all protons in PPPA and PPPW were allocated to the number of protons in their above-mentioned molecular formulae, and the number of hydroxyl groups present in the polymer molecules are listed in Table V.

Carbonyl group was noticeably observed in IR and NMR spectra, but the assignment determined only ketons. Quantitative determination of the carbonyl group was carried out by means of hydrazone formation with 2,4-dinitrophenylhydrazine followed by elemental analysis of nitrogen. The results obtained as numbers of $\text{C}=\text{O}$ group in both polymers were also listed in Table V. The values seemed to be small in contrast to the strong absorption band appearing in the IR spectra, but this conflict was understandable because the IR spectrum was highly sensitive to the polar atom group. The hydrazone of PPPA was reddish brown and that of PPPW was yellowish brown. It was known that 2,4-dinitrophenylhydrazones were generally yellow-colored, but when the carbonyl group was conjugated with $\text{C}=\text{C}$ or aryl group, the hydrazone showed reddish orange color.¹⁰ The presence of conjugated carbonyl system in the polymer was acceptable in consideration of the chemical structure of the starting monomer.

The spectrometric interpretation revealed that the triple bonds in the monomer were all consumed for the plasma polymerization, and only the double bond was found in the resulting polymers. The double bond would have been further rearranged for chain propagation, branching, and crosslinking during the plasma polymerization. Measurement of the unsaturated bond was useful to know the process of polymerization. The olefinic unsaturation of PPPA and PPPW was determined by use of the Wijs method in which

TABLE V
Quantitative Analysis of Functional Groups in PPPA and PPPW

Function	PPPA	PPPW
Hydroxyl	4	7-8
Carbonyl	1	2
Olefinic unsaturation	2-3	1-2

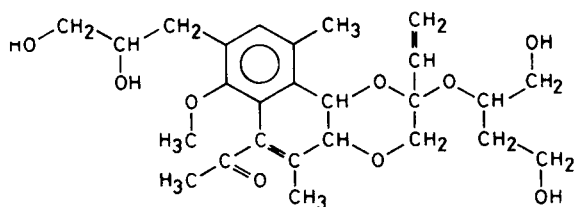
smoother reaction underwent compared with the bromination.⁵ The reaction time had to be longer than ordinary process, because of its crosslinked and 3-dimensional molecular structure. Potentiometric finish should be used for titration of iodine because methanol as a solvent of the polymers strongly interfered with a color indicator. Numbers of olefinic unsaturation per unit molecule were calculated for PPPA and PPPW and are listed in Table V.

Numbers of alicyclic structure were calculated by subtracting the number of carbonyl group, olefinic unsaturation, and double bonds in the aryl group from the degree of unsaturation. PPPA could involve one aryl group which was assigned in the NMR spectrum and one to two alicyclic groups in a unit molecule. Therefore, PPPA having the average molecular weight contained five to six unsaturated bonds. PPPW was found to have no aryl group on the basis of IR and NMR spectra but involved eight to nine alicyclic groups. The results of these calculations indicated that PPPA preserved an abundance of double bonds while PPPW left a few. The reason was interpreted as follows: Under the same pressure and electric power, the water molecules in PW monomer gas decreased the cross section of electron collision because of the smaller diameter than that of PA molecule. Therefore, the average kinetic energy of electrons would be higher in the PW plasma than in the PA plasma. In the former plasma, the reaction intermediates involving the double bonds would be further rearranged consuming the double bonds to yield a polymer of fewer unsaturation sites. Such a conjecture was in good agreement with an increase of deposition rate of the polymer due to an increase of water content in PA monomer.⁴

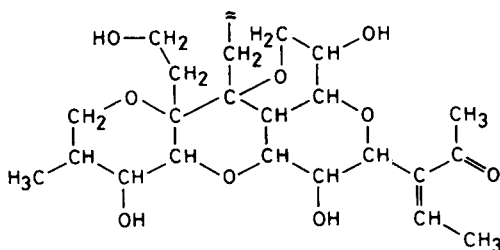
Chemical Structure of PPPA and PPPW

All results of the analyses described above made it possible to draw illustrative chemical structures of PPPA and PPPW at the average molecular weight. A trial is proposed as shown in Figure 7. It should be noticed that the plasma polymers have wide distributions of molecular weight as well as varieties of chemical composition, and both the characters are changeable depending upon operating conditions, e.g., high-frequency power, pressure, flow rate of monomers, and so forth. Therefore the illustrative chemical structures presented here are only symbolic models which were consistent with the various analytical data and were helpful to understand physicochemical properties of the given polymers.

The model structure of PPPA seemed to be relatively flat in contrast to the other plasma polymers reported.¹¹⁻¹⁵ A stereo model composed in accordance with the illustration of Figure 7 measured 8.5 Å in width and 18 Å in length. There were some free rotation sites such as C—C and C—O in the side chains. Therefore, the whole molecular structure of PPPA seemed to be flexible. This model was based on the average molecular weight listed in Table V, which was measured with the methanol-tetrahydrofuran extract. Remembering the extract as a 63% fraction of probably lower molecular species in the intact polymer, the model structure of PPPA in Figure 7 might be better illustrated to be roughly twice as large.



PPPA



PPPW (1/2)

Fig. 7. Symbolic representation of chemical structures of plasma polymers.

A stereo model of PPPW in accordance with Figure 7, which illustrates one half of the molecule, was rather 3-dimensional, and its principal alicyclic frames involved participation of oxygen atoms. These oxygen atoms were supposed to be distributed uniformly within the molecular structure during the polymerization process. The free rotation sites were also found as in the case of PPPA. The half part of the unit molecule measured 6–7 Å in width and 12–14 Å in length, which was relatively compact as compared with PPPA. Many hydroxyl groups were prominent outside of the molecule demonstrating the hydrophilic property.

Table V also shows that the ratio of hydroxyl groups to carbon atoms in PPPA ($C_{26}H_{36}O_9$) and PPPW ($C_{44}H_{66}O_{18}$) were similar. The reason for the significant difference of their physicochemical properties such as solubility to methanol and contact angle⁴ may be briefly explained as follows: (1) Hydrophilic property is dependent not only on hydroxyl groups but also on other polar groups involving carbonyl and etheric oxygen atoms. PPPW contains much higher content of oxygen than PPPA. (2) The data of PPPA were derived from the methanol extract of the polymer, which was 63% fraction probably of a lower molecular weight. It was suggested that the insoluble higher molecular fraction exhibits fairly lower polarity than the methanol extract. The significant difference between the contact angles on the intact PPPA and PPPW films was therefore understandable.

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