

Spectroscopic Elucidation of Chemical Structure of Plasma-Polymerized Pyridine

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Synopsis

Chemical structure of the plasma-polymerized pyridine film produced on a glass reactor wall by means of the plasma technique in which the pyridine vapor was electronically excited by high-frequency power under a reduced pressure was elucidated. The polymer was highly hydrophilic and was soluble to some of the polar organic solvents so that nitrogen-containing polar functional groups were predicted to participate in the chemical structure of the polymer molecules. $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and IR spectroscopies, high-resolution mass spectral data, and number-average molecular weight determination with some aid of microelemental analysis revealed the presence of various functional groups such as imine, nitrile, amine, pyridine ring, its *N*-oxide, and even amide. The oxygen atoms involved in the last two groups were supposedly introduced by contact with ambient air after the plasma process. The hydrophilic nature of the polymer which was essential for preparing reverse osmosis membrane was therefore due to the overall hydration effect of these polar functional groups.

INTRODUCTION

Vapors of various organic compounds can be readily polymerized by subjecting them to a glow discharge under a reduced pressure, where deposition of polymer thin film proceeds with a slow rate of growth onto a surface of solid substrate preliminarily placed in the glow discharge region.¹⁻⁵ The polymer thin film covers the substrate with uniform and controlled thickness of 100–10000 Å being featured by pinhole-free characteristic, so that application of the plasma polymerization have been currently attempted to surface modifications of solid materials employing various monomer compounds having either hydrophobic or hydrophilic nature⁶⁻¹⁰ and at the same time to preparations of semipermeable membranes formed on porous filter materials.¹¹⁻¹⁷ The latter technique has been mostly studied for reverse osmosis membrane because of predicted features of extremely thin and pinhole-free film by which a high degree of salt rejection and water permeability was anticipated under a high pressure of operating condition.

While the plasma technology of preparing reverse osmosis membrane is still extensively under way, very little information has been reported in terms of hydrophilic functional groups retained in the polymer matrices which act as the reason of reverse osmosis. Yasuda and his co-workers^{12,13} found that nitrogen-containing monomers generally yielded successful results in comparison with oxygen-containing ones, probably because a considerable amount of oxygen atoms might be eliminated from the polymer during the highly excited plasma process forming thermodynamically stable fragments such as OH· and CO·

radicals. Therefore, they recommended some pyridine homologs as the monomers for preparing membranes of high performance, but practically no information was presented for the hydrophilic functional groups retained in the resulting polymers. Bell, Hollahan, and their co-workers¹⁴⁻¹⁶ followed the work with aliphatic amines and found that the polymers contained nitrogen functional groups mostly as imine type and, to a less extent, as amine and nitrile types. Their analysis of the polymer was carried out essentially by means of IR spectroscopy with some aid of ESCA.

This paper presents some details of chemical structure of the plasma-polymerized pyridine (PPP) by which basic knowledge of the transformation of the nitrogen bond in the monomers of pyridine homologs towards those in the polymer can be obtained, although we have published a brief account of the result elsewhere.¹⁸ Structural elucidation of PPP employing ¹H-NMR, ¹³C-NMR, and IR spectroscopies, high-resolution mass spectral data, and number-average molecular weight determination with some aid of microelemental analysis have revealed the presence of various functional groups such as imine, nitrile, amine, pyridine ring, its *N*-oxide, and even amide. The oxygen atoms involved in the last two groups were supposedly introduced by contact with ambient air after preparation of the plasma polymer. The reason of reverse osmosis exhibited by membranes of plasma-polymerized pyridine and its homologs may be therefore due to the overall hydration effect of these polar functional groups.

EXPERIMENTAL

Plasma System

A schematic diagram of the apparatus is shown in Figure 1, which is practically the same as described in the previous paper.¹⁹ A pyrex glass chamber having a diameter of 7 cm and a length of 30 cm was installed in vertical position and could be evacuated from the bottom by a rotary pump via a cold trap. A MacLeod gauge monitored the pressure in the chamber during the plasma process. An argon flow was introduced from the top of the chamber while the flow

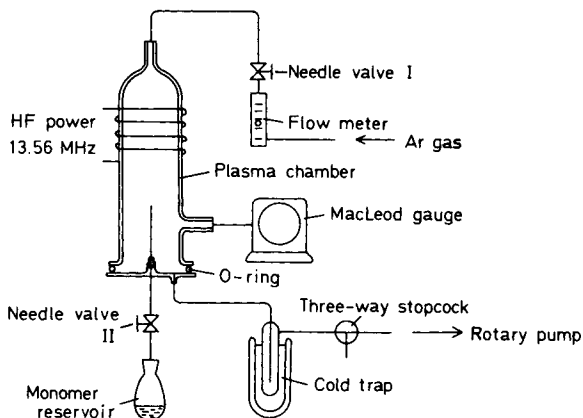


Fig. 1. Schematic diagram of plasma-polymerization apparatus.

rate was controlled by a flow meter and the needle valve I. Pyridine was reserved in an egg-shaped flask so that its vapor pressure gently supplied the monomer gas from the bottom of the chamber via the other needle valve II. Homogeneous dilution of the pyridine vapor with the argon gas was ensured by effective counter diffusion under the low pressure. Plasma polymerization was initiated by loading high-frequency (HF) electric power of 13.56 MHz to a HF coil wound around the plasma chamber.

Monomer

Dry pyridine was purified by vacuum distillation. The distillate was immediately charged into the monomer reservoir which was rolled up by an aluminum foil to prevent coloring of the monomer if it were exposed to light.

Procedure of Plasma Polymerization

Closing the two needle valves of the plasma apparatus, the plasma chamber was evacuated by the rotary pump until the MacLeod gauge indicated the pressure of 0.005 mm Hg. Argon was then introduced to the chamber by opening the needle valve I so as to adjust the pressure at 0.05 mm Hg. Shortly later, the pyridine vapor was drawn into the chamber by gentle opening of the needle valve II and kept for 20 min until no air came out of the reservoir and at the same time the pressure in the chamber was raised to approximately 1 mm Hg.

Glow discharge was then initiated by loading HF power of 35 W while the total pressure in the chamber fell down to 0.6 mm Hg due to the intense polymerization of the monomer undergoing within the discharge region. Blue light emission was observed from the discharged gas. The vapor pressure of pyridine was cited to be 20 mm Hg at 25°C, so that enough rate of pyridine vapor could be supplied to the plasma chamber employed in this experiment.

The plasma polymerization was continued for 5 min until the HF power was turned off and the needle valve II was closed. The rotary pump was then turned off, but the argon flow was increased to fill up the plasma chamber until the pressure reached to 1 atm within 1 h. The polymer was always deposited onto the inside wall of the plasma chamber to the full extent of discharge region forming solid film, and no oily product nor powder material was obtained so far as the operating conditions described above were followed. The polymer film was left standing in the argon atmosphere for overnight in order to terminate the free radicals retained in the polymer matrix as much as possible. Some possible survivals of the free radicals would be air-oxidized when the polymer was taken out of the plasma chamber. The polymer film was dissolved in acetone by repeated rinsing of the plasma chamber and the acetone solution was evaporated to obtain 50–70 mg of the polymer material, which was finally dried *in vacuo* and powdered.

Molecular Weight Determination

Number-average molecular weight of PPP was determined by the Knauer Dampdruck Osmometer using benzil ($C_{14}H_{10}O_2$) as a standard material and pyridine as a solvent under a preset temperature of 60°C.

Spectroscopies

IR Spectra. Powdered PPP was subjected to the IR spectroscopy using the Shimadzu IR-400 Spectrophotometer by means of the KBr disk method.

$^1\text{H-NMR}$ Spectra. The Varian XL-200 (200 MHz) was employed for the measurement of $^1\text{H-NMR}$ spectra of PPP in solvents of CD_3COCD_3 (2 mg in 1 mL) and CF_3COOD (5 mg in 1 mL) using TMS as a reference material. Chemical modifications such as methyl esterification and acetylation were applied to PPP, and the resulting derivatives were also subjected to $^1\text{H-NMR}$ spectroscopy using the Varian CFT-20 (80 MHz) in CF_3COOD (20 mg in 1 mL for the former derivative, 30 mg in 1 mL for the latter).

$^{13}\text{C-NMR}$ Spectra. The Varian XL-200 (50 MHz) was employed for the measurement of $^{13}\text{C-NMR}$ spectra of PPP dissolved in deuteropyridine (500 mg in 1 mL) for the search of the carbonyl group and in phosphoric acid (150 mg in 1 mL) for quantitative evaluation of carbon atoms participating in the whole molecular structure under the operating mode of gated decoupling.

High-Resolution Mass Spectra. Powdered PPP was analyzed by the Hitachi Mass Spectrometer.

Solubility Test in Organic Solvents

Powdered PPP weighed in a range of 15–20 mg was shaken with 5 mL of various organic solvents in a preweighed centrifuge tube for 10 min and left standing for 30 min. Centrifugation at 1500 rpm was continued for 15 min and the supernatant was carefully removed by a capillary pipet. After drying *in vacuo*, insoluble residue was measured by reweighing the centrifuge tube.

Chemical Modifications of Polar Functional Groups

Methyl Esterification. The nitrile group in PPP was methylesterized and monitored by IR and $^1\text{H-NMR}$ spectroscopies. A 40 mg of PPP was dissolved in 4 mL of $\text{MeOH-H}_2\text{SO}_4$ (3:1) and the solution was heated at 80°C for 10 h. After cooling to room temperature, 10% NaOH solution was added for neutralization. The precipitate was collected after centrifugation at 1500 rpm for 15 min, washed by distilled water, and finally dried.

Acetylation. Amine groups of PPP were acetylated by dissolving 60 mg of the polymer in 3 mL of pyridine to which 0.3 mL of acetic anhydride was added. After heating at 90°C for 4 h, the solution was poured into 10 mL of ice water and left at room temperature for a while. The precipitate was collected and dried at 60°C under a reduced pressure.

Reaction with Carbon Disulfide. Another type of chemical modification for amine groups was undertaken by dissolving 30 mg of PPP in 2 mL of pyridine, to which 2 mL of carbon disulfide was added. Since the reactions proceed with the same stoichiometry for primary and secondary amines at room temperature but with different ways at elevated temperature, quantitative analysis of the individual amine groups might be possible by calculation. The solution was therefore divided into two portions, one of which was heated at 90°C for 2 h and immediately evaporated before the residue was dried at 60°C , the other of which was left standing at room temperature for a week and treated as above except

drying at room temperature. The two products were subjected to sulfur determination by means of the oxygen-flask method where microscale samples were ignited and the combustion gases were absorbed in 5 mL of H_2O_2 solution. Sulfate ion derived from the respective sample was titrated by 0.005M $BaCl_2$ solution with a potentiometric finish using the Metrohm Potentiograph E536-E575-E549 incorporated with the Corning Sodium-Selective Glass Electrode as an end point indicator.²⁰⁻²²

Trifluoroacetylation. Amide proton was slowly substituted by a strong acylation agent, *N*-methyl-bis(trifluoroacetamide),²³ inconsistently with the milder agent, acetic anhydride, so that 150 mg of PPP dissolved in 4 mL of pyridine was reacted with 0.3 mL of the former agent. The mixture was heated at 90°C for 4 h. After cooling to room temperature, the solution was evaporated, and the residue was dried at 50°C. The resultant material was subjected to fluorine determination also by means of the oxygen-flask method. Fluoride ion thus obtained was determined spectrophotometrically in the conventional manner using the alizarin complexone reagent.

Benzenesulfonylation. A reaction similar to trifluoroacetylation was applied to PPP using benzenesulfonyl chloride as an alternative. To a solution of 60 mg of PPP in 2 mL of pyridine was added 0.1 mL of benzenesulfonyl chloride and the reaction mixture was heated at 90°C for 4 h. The mixture was then evaporated, and the residue was dried at 80°C under a reduced pressure. Sulfur atoms introduced in the derivative were determined by the oxygen-flask method.

Neutralization of Basic Nitrogen Atoms

The number of basic nitrogen atoms in PPP having the average molecular weight was determined by neutralization of the polymer sample in nonaqueous medium, i.e., a 1.5 mg of the sample was dissolved in glacial acetic acid and was titrated by 0.01M perchloric acid in the same solvent, while the Horiba pH Meter M-7 was employed for monitoring the end point of the titration.

RESULTS AND DISCUSSION

Solubility of PPP in Organic Solvents

The polymer film firmly deposited onto the inside wall of the plasma chamber was entirely soluble in acetone, which had a low boiling point (56.5°C/760 mm Hg) so as to be evaporated readily from the polymer solution to recover the whole polymer material. The solubility test of the polymer was then carried out for other organic solvents having different polarities, and the result is tabulated in Table I.

Polar solvents as well as acidic solvents effectively dissolved the polymer with an exception of alcohols so that polar and basic characters were predicted for the polymer. It was also necessary to know several good solvents other than acetone because NMR spectroscopy and chemical modifications of the polymer called for different solvents suitable for their individual principles.

TABLE I
Solvent Extraction of Plasma-Polymerized Pyridine

Solvent	Dielectric constant	Extract/polymer (%) ^a
Dimethylsulfoxide	48.9	100
Trifluoroacetic acid	39.5	100
Methyl alcohol	32.7	44
Ethyl alcohol	24.3	28
Acetone	20.7	100
Pyridine	12.3	100
Acetic acid	6.15	100
Chloroform	4.81	38
1,4-Dioxane	2.21	78
Nonpolar solvents		0

^a Wt % of soluble fraction from the plasma polymer.

Chemical Formula at Average Molecular Weight

Molecular weight determination was carried out with the acetone extract which was redissolved in acetone to have known concentration. Vapor pressure osmometer was then operated to derive the number-average molecular weight of the polymer referring to a calibration curve of molar concentration preliminarily established by a standard material. The result gave $M_w = 900$, while large distribution of the molecular size was supposed as the common character of the plasma-polymerized materials.

The same experiment was concomitantly carried out with a polymer sample which was directly scraped off from the polymer film deposited in the plasma chamber and immediately dissolved in acetone to have known concentration. The result obtained was practically the same as in the case of acetone extract so that no appreciable change of molecular structure was supposed during the time-consuming process of solvent evaporation and vacuum drying under the elevated temperatures.

Samples of the acetone extract and the film polymer directly scraped off from the plasma chamber were subjected to microelemental analysis to determine C, H, N, and O. The results are tabulated in Table II. The presumable chemical formula at the average molecular weight were calculated and also listed in the same table.

TABLE II
Determination of Chemical Formula at Average Molecular Weight

	Film polymer (%)	Acetone extract (%)
Microelemental analysis	H 5.50	H 5.50
	C 74.49	C 73.54
	N 16.01	N 15.62
	O 4.00	O 5.34
Experimental formula	$C_{5.4}H_{4.8}N_{1.0}O_{0.2}$	$C_{5.5}H_{4.9}N_{1.0}O_{0.3}$
Molecular formula	$C_{54}H_{48}N_{10}O_2$	$C_{55}H_{49}N_{10}O_3$

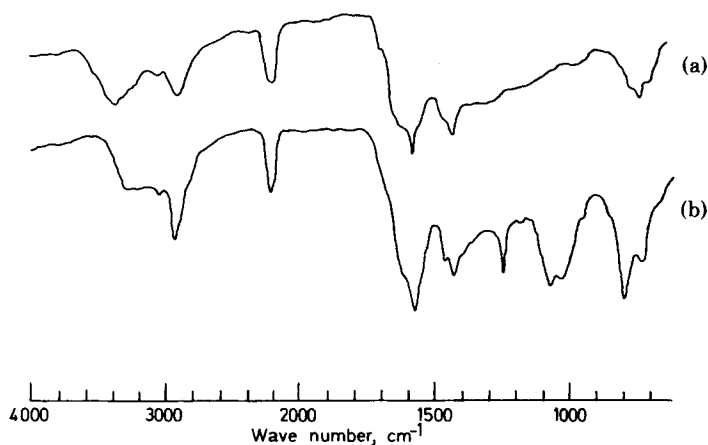


Fig. 2. IR spectra of plasma-polymerized pyridine: (a) acetone extract; (b) chloroform extract.

It has been often observed that some oxygen atoms were introduced in the plasma polymers when the materials were exposed to air after the plasma process, so that the oxygen values in Table II are understandable in spite of dealing with the monomer having no oxygen component.^{15,19} However, one more oxygen per molecule was involved in the acetone extract than in the film polymer which was directly scraped off from the plasma chamber. It was therefore postulated that some radical sites were left alive in the interior of solid particles derived from the film polymer while the exterior was oxidized by exposure to atmospheric oxygen, whereas all the radicals in the polymer were oxidized when the film polymer was dissolved in acetone.

There was also a question whether the introduction of the additional oxygen component resulted from the reaction between the polymer radical and the acetone or whether it was just from the air oxidation. Comparative study of the IR spectrum of the film polymer with that of the acetone extract was unsuccessful, because the former spectrum was practically the same as the latter which is shown in Figure 2(a), so that an attempt was made to alter the solvent for extraction from acetone to chloroform.

The chloroform extract showed some characteristic absorption bands at 1250, 1080, and 790 cm^{-1} in reference to the spectrum of the acetone extract as illustrated in Figure 2(b). The bands were assigned to C—Cl stretch and bend, so that more or less chemical reaction between the polymer and the solvent was suggested. Elemental analysis of chlorine in the chloroform extract found one atom of chlorine in one molecule of the average molecular weight; therefore, it was likely true that the acetone also reacted with the polymer to a certain extent.

Either of the molecular formula, $\text{C}_{55}\text{H}_{49}\text{N}_{10}\text{O}_3$ for the acetone extract or $\text{C}_{54}\text{H}_{48}\text{N}_{10}\text{O}_2$ for the film polymer, suggested that the PPP was approximately 11-mer, but one nitrogen atom per molecule was eliminated. The fact of nitrogen elimination was explained by partial fragmentations of the monomer to amino, cyanide, and other nitrogen-containing radicals in the highly excited plasma space. An abundance of atomic hydrogen split off from the monomer seemed

to enhance such reductive reactions, and this was partly approved by appreciable shortage of hydrogen atoms in PPP as compared with the initial monomer material.

IR Spectrum

IR spectrum of the acetone extract shown in Figure 2(a) was almost the same as that of the film polymer, but a small absorption band at 1700 cm^{-1} was noted with regard to the acetone extract. The band was assigned to the carbonyl group, which was likely introduced by the reaction between the polymer and the solvent.

Whole assignments of the IR spectrum of the acetone extract are tabulated in Table III while eliminating the band at 1700 cm^{-1} derived from the reaction with solvent. The table suggests the presence of nitrile, amine, pyridine ring, imine, and amide groups in PPP as the functional groups containing nitrogen atoms. The absorption bands of the C—H bend suggested that the substitutions of the pyridine ring were mostly confined to α -positions. Pyridine rings and other functional groups were ascertained and quantitatively determined by means of $^1\text{H-NMR}$ and some chemical modifications as the following.

$^1\text{H-NMR}$ Spectra

Figure 3(a) shows the $^1\text{H-NMR}$ spectrum of the acetone extract in CD_3COCD_3 in which resonance peaks arising from the protons on pyridine rings spread within a range of 9.0–6.5 ppm involving three main peaks at 8.6 ppm, 7.8 ppm, and 7.4 ppm. Three peaks were assigned to α -, γ -, and β -positioned protons, respectively, since nonsubstituted pyridine exhibits its resonance peaks at 8.5 ppm (α -protons), 7.4 ppm (γ -proton), and 7.2 ppm (β -protons).

The ratio of the peak areas in this region was $A:(B + C) = 3:10$, where A , B , and C denoted the numbers of α -, β -, and γ -protons, respectively, while a broad

TABLE III
Assignment of Infrared Absorption Bands

Absorption band (cm^{-1})	Assignment
3350	N—H stretch
3060	C—H stretch in pyridine ring
2900	C—H stretch in methylene and methyl groups
2200	C \equiv N stretch
1640	C=C stretch in olefine N—H bend C=O stretch in amide
1585	C=N stretch C=C stretch in pyridine ring
1460	C—H bend in methylene group
1430	C—H bend in methyl group
960	C—H out-of-plane deformation in —C=C— (<i>trans</i>)
780, 720	C—H bend in 2,6- or 2,3-disubstituted pyridine
750	C—H bend in 2-monosubstituted pyridine

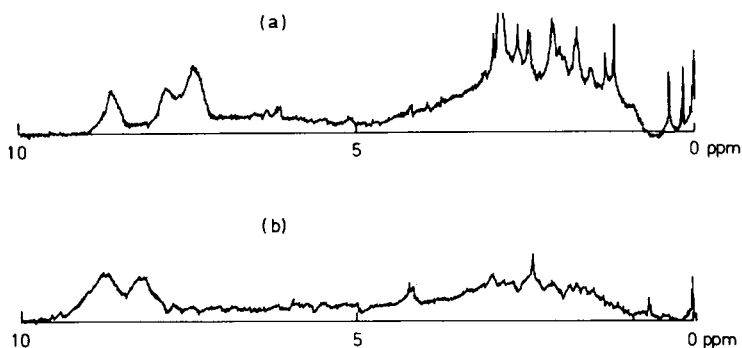


Fig. 3. $^1\text{H-NMR}$ (100 MHz) spectra of plasma-polymerized pyridine: (a) CD_3COCD_3 medium; (b) CF_3COOD medium.

peak at 7.0–6.5 ppm was ignored. This quantitative evaluation suggested that α -position was preferentially substituted. There was also an interesting aspect on chemical shifts induced by the change of solvent acidity, i.e., the γ - and β -protons moved to lower field in CF_3COOD , as illustrated in Figure 3(b).²⁴ The γ -proton moved to a greater extent than the β -protons, so that the γ -proton was separated from the β -protons and even entirely overlapped with the α -protons. It followed therefore that the resonance peak of β -protons could be quantitatively evaluated in reference to the overlapping peak of α - and γ -protons. The ratio was $(A + C):B = 7:6$, while a broad peak appearing at 7.8–7.2 ppm was ignored.

Based on these spectral data and the molecular formula, the number of protons belonged to pyridine rings in one molecule was calculated to be 15; therefore four pyridine rings were predicted in which three 2-monosubstituted rings and one 2,6-disubstituted ring were involved. The NMR results were consistent with the IR spectrum.

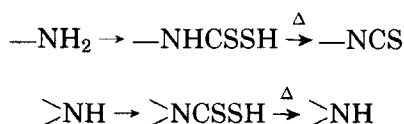
Esterification of Nitrile Group

The presence of the nitrile group in PPP was obvious in IR spectrum, but the polymer was further treated with $\text{CH}_3\text{OH-H}_2\text{SO}_4$ on heating for 20 h by which the nitrile group was methyl-esterified. The completion of the reaction was monitored by extinction of the absorption band of $\text{C}\equiv\text{N}$ in IR spectrum. The $^1\text{H-NMR}$ spectrum of the resultant methyl ester of the acetone extract suggested three carboxymethyl groups in one molecule as a result of a calculation referring to the number of protons belonging to the pyridine rings. However, it should be noticed that the primary amide group, if present, would be also methyl-esterified. While the elemental analysis and the IR spectrum supported the existence of an oxygen atom as amide carbonyl, it would be reasonable to allocate one carboxymethyl group to be derived from the amide group and other two carboxymethyl groups from the nitrile. Further details of the IR and $^1\text{H-NMR}$ spectra implied that these three carbonyl groups were conjugated to unsaturated bonds at α,β -position, since the ester carbonyl stretch in IR spectrum appeared at 1720 cm^{-1} and the carboxymethyl signal indicated their resonance peak at 4.0–3.8 ppm.

Acylation of Amine Groups

Since the primary and secondary amine groups involving active protons are susceptible to acylation, the acetone extract was treated with acetic anhydride in a pyridine medium. The number of acetyl groups introduced was calculated from the $^1\text{H-NMR}$ spectral data, i.e., acetyl protons were quantitatively determined by referring to an area standard of the pyridine protons in the polymer. The result gave 1.5 acetyl groups in one molecule of the average molecular weight.

Separative determinations of the primary and secondary amine groups were attempted, taking advantage of different stoichiometries in the course of reactions with carbon disulfide. The primary amines are rapidly converted to dithiocarbamate, which are further transformed to isothiocyanate by being left at room temperature for a long time²⁵ or by heating, whereas the secondary amines are also rapidly converted to dithiocarbamate, but are rapidly decomposed to the initial secondary amine by heating. These reactions are summarized as follows:



The presence of the primary amine group in PPP was simply ascertained by an absorption band of 2070 cm^{-1} assigned to an $-\text{NCS}$ stretch in the IR spectrum of the reactant. An additional qualitative test of the primary amine group was carried out by applying carbylamine reaction in which chloroform selectively reacted with the primary amine in an alkaline medium evolving a disagreeable odor of isonitrile.

Determination of sulfur in the foregoing reactant which were treated with heat made it possible to evaluate the number of the primary amine group in PPP, while the same determination for the reactant obtained by leaving at room temperature for a long time suggested the number of secondary amine group. Oxygen-flask combustion followed by the barium titration using a sodium-selective glass electrode as an end-point indicator²² brought a result of 1.67% sulfur in the former reactant and the value was nearly one-half of an assumption that

TABLE IV
Chemical Modifications of Functional Groups

Modification	Reaction formula	Groups/molecule
Carboxy methylation	$\left. \begin{array}{l} -\text{C}\equiv\text{N} \\ -\text{CONH}_2 \end{array} \right\} \rightarrow -\text{COOCH}_3$	3.0
Acetylation	$\left. \begin{array}{l} -\text{NH}_2 \rightarrow -\text{NHCOCH}_3 \\ >\text{NH} \rightarrow >\text{NCOCH}_3 \end{array} \right\}$	1.5
Reaction with CS_2	$-\text{NH}_2 \rightarrow -\text{N}=\text{C}=\text{S}$	0.5
	$>\text{NH} \rightarrow >\text{NCSSH}$	1.0
Trifluoroacetylation	$\left. \begin{array}{l} -\text{NH}_2 \rightarrow -\text{NHCOCF}_3 \\ >\text{NH} \rightarrow >\text{NCOCF}_3 \\ -\text{CONH}_2 \rightarrow -\text{CONHCOCF}_3 \\ -\text{CONH}- \rightarrow -\text{CONCOCF}_3 \end{array} \right\}$	2.4

one primary amine group would exist in one molecule of the average molecular weight, i.e., one primary amine group actually existed in two molecules of PPP. Determination of the latter reactant resulted in 8.09% sulfur, which suggested roughly one secondary amine group in one molecule. Summation of the number of primary and secondary amine groups was also consistent with the number of acetyl group (1.5) introduced by the acetylation of PPP.

It was of interest to know that the primary and secondary amine groups in PPP derived from the ring-opening of pyridine monomer likely participated in the hydrophilic power of the polymer and at the same time fairly intense hydrogenation of the nitrogen atom in the reaction intermediates took place during the plasma polymerization.

Acylation of Amine and Amide Groups

N-methyl-bis(trifluoroacetamide), the strong acylation agent as mentioned above, reacts not only with amine protons but also with amide ones.²³ The IR spectrum of the trifluoroacetyl-PPP obtained from the reaction in the pyridine medium demonstrated an introduction of new absorption bands, namely, a strong C=O stretch (1700 cm^{-1}) and C—F stretch ($1100\text{--}1200\text{ cm}^{-1}$). Determination of fluorine in the same material by the oxygen-flask method gave a result of 11.8% in weight. The value could be transformed to be 2.4 trifluoroacetyl groups in one molecule of the average molecular weight.

A similar experiment was carried out using benzenesulfonyl chloride as a substitution agent. The resultant material was subjected to the oxygen-flask method for determination of sulfur and the result suggested an introduction of 2.3 benzenesulfonyl groups by which the result of the former experiment was approved.

TABLE V
High-Resolution Mass Spectral Data of PPP

Peak number	Relative intensity	m/z	Composition
1	40.8	92.05417	C ₆ H ₆ N
2	100.0	93.04170	C ₅ H ₅ N ₂
3	39.6	104.04452	C ₇ H ₆ N
4	34.4	105.04443	C ₆ H ₅ N ₂
5	7.8	108.05780	C ₆ H ₆ N ₃
6	52.2	117.04575	C ₇ H ₅ N ₂
7	62.3	118.05633	C ₇ H ₆ N ₂
8	55.4	130.05402	C ₈ H ₆ N ₂
9	35.4	142.04798	C ₉ H ₆ N ₂
10	23.4	154.04990	C ₁₀ H ₆ N ₂
11	6.4	165.03743	C ₁₁ H ₅ N ₂
12	33.5	168.04755	C ₁₀ H ₆ N ₃
13	12.2	133.03748	C ₇ H ₅ N ₂ O
14	15.0	159.06460	C ₉ H ₇ N ₂ O
15	27.1	170.04586	C ₁₀ H ₆ N ₂ O
16	26.2	171.06206	C ₁₀ H ₇ N ₂ O
17	19.6	184.05840	C ₁₁ H ₈ N ₂ O
18	12.3	185.05826	C ₁₀ H ₇ N ₃ O

Constituent of Hydrophilic Functional Groups in PPP

The presence of various functional groups presumed by means of the foregoing chemical modifications are summarized in Table IV. Based on the analytical result of amine groups, approximately one amide in one molecule of PPP was supposed. Such reasoning was also approved by ^{13}C -NMR and high-resolution mass spectra. In the ^{13}C -NMR spectrum was observed a small but marked resonance peak of amide carbons at 175–165 ppm while the high-resolution mass spectrum gave signals of $m/z = 44.0156$ (assigned to $\cdot\text{CONH}_2$) and $m/z = 71.03568$ (assigned to $\text{CH}_2=\text{CHCONH}_2$), by which the presence of primary amide was exclusively suggested.

Constitution of the overall hydrophilic functional groups containing nitrogen atoms was therefore made clear, i.e., one molecule of PPP having the average molecular weight (acetone extract, $\text{C}_{55}\text{H}_{49}\text{N}_{10}\text{O}_3$) involved the atom groups of four pyridine rings, two or three nitriles, zero or one primary amine, one secondary amine, and one primary amide. There would be other minor functions such as tertiary amine and imine groups faintly observed in IR spectrum (Table III), but no further analysis was followed due to the lack of active protons.

Whole Molecular Structure of PPP

As for the structural details around the pyridine rings in the polymer network, high-resolution mass spectral data offered intriguing information, as listed in Table V. First, some of the pyridine rings were substituted by unsaturated carbon chain and others by nitrogen atom (peak numbers 1–5). Secondly, some of the pyridine rings linked each other forming dipyridyl group (peak numbers 6–12). Thirdly, some of the dipyridyl group were oxidized to be *N*-oxide type (peak numbers 13–18). Such assumptions were approved by high degree of unsaturation in mass spectral data of these fragments having two or three nitrogen atoms and by the disintegration stepped in a similar manner as pyridine behaves.²⁶ Possible partial structures surrounding the pyridine rings in PPP are summarized in Figure 4, where positions of substitution have been determined by the IR and the ^1H -NMR spectra.

^1H -NMR spectroscopy particularly brought a valuable information that some α -carbons of pyridine rings were substituted by nitrogen atoms because of high-field shift (7.0–6.5 ppm) of β -position protons,²⁷ although the same protons of pyridine *N*-oxide were excluded. The evaluation of peak area ratio of these

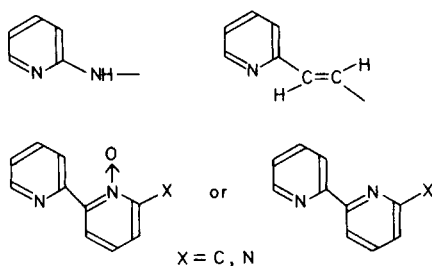


Fig. 4. Types of α -substitution on pyridine ring.

TABLE VI
 Chemical States and Abundances of Carbon Atoms Participating in Structure of PPP

State of carbon atom	Abundance
Carbonyl carbon	4 ^a
sp ² carbon	37 (pyridine ring: 20)
sp carbon	2
sp ³ carbon	12 $\left[\begin{array}{l} \text{—CH}_3 \quad 3 \\ \text{—CH}_2\text{—} \quad 6 \\ \begin{array}{c} \\ \text{—CH—} \quad 2 \\ \\ \text{—C—} \quad 1 \\ \end{array} \end{array} \right]$

^a Nitrile carbons hydrolyzed in phosphoric acid medium were involved.

β -position protons and the total protons in PPP resulted in two β -position protons of nitrogen-substituted pyridine rings at α -position.

The information for the carbon skeleton were finally revealed by ¹H-NMR and ¹³C-NMR spectroscopies. The ratio of the peak areas, measurable in a ¹³C-NMR spectrum chart, was satisfactorily accurate, because the spectroscopy was operated under the condition of gated decoupling with long pulse intervals of 15 s (solvent; phosphoric acid).

In terms of the ¹H-NMR spectrum, peaks were divided into three ranges: 9.0–6.5 ppm (pyridine ring protons), 6.5–4.5 ppm (olefine protons), and 4.5–0.8 ppm (alkane protons and active protons). The ratio of peak areas in the three regions was 15:10:25. The peaks of alkane protons were further divided into four

narrower ranges: 4.5–2.5 ppm ($\begin{array}{c} | \\ \text{—CH—} \\ | \end{array}$ and $\text{—CH}_2\text{—}$), 2.5–1.5 ppm ($\begin{array}{c} | \\ \text{—CH—} \\ | \end{array}$, $\text{—CH}_2\text{—}$, and —CH_3), 1.5–1.2 ppm ($\begin{array}{c} | \\ \text{—CH—} \\ | \end{array}$ and —CH_3), and 1.2–0.8 ppm (—CH_3). The ratio of peak areas was 11:8:3:3.

The ¹³C-NMR spectrum peaks of PPP could be also divided into four ranges: –165 ppm (carbonyl carbon partly involving those derived from hydrolysis of nitrile carbon in a solvent of phosphoric acid), 160–100 ppm (sp² carbons in pyridine rings and olefinic unsaturations), 100–70 ppm (sp carbon in alkyne), and below 70 ppm (sp³ carbons in alkanes). The ratio of peak areas was 4:37:2:12. Since the presence of four pyridine rings were predicted in one molecule having the average molecular weight as mentioned above, a coarse calculation made it possible to suppose eight or nine olefinic double bonds involved in the same molecule. Further detail of the sp³ carbon range was elucidated by assignment of five narrower ranges such as 70–60 ppm (quaternary carbons), 60–40 ppm (quaternary, methyne, and methylene carbons), 40–25 ppm (quaternary, methyne, methylene, and methyl carbons), 25–15 ppm (methylene and methyl carbons), and 15–10 ppm (methyl carbons). The ratio of peak areas was 1:4:3:3:1.

An algebraic calculation based on the data of peak area ratios in ¹H-NMR and ¹³C-NMR spectra together with the number of amine and amide groups in one molecule enabled us to predict the chemical states and abundances of carbon atoms in PPP, as are summarized in Table VI. The formation of methylene, methyl, and amine groups from the pyridine monomer with concomitant elimi-

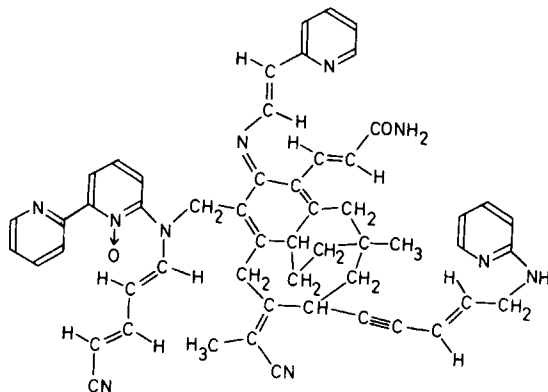


Fig. 5. Predicted chemical structure of plasma-polymerized pyridine.

nation of nitrogen and hydrogen atoms suggested that intense reducing reactions took place during the plasma polymerization.

The degree of unsaturation which evaluates the shortage of hydrogen (H_2) in reference to a hypothetical alkane having the same number of carbon atoms as the polymer was calculated, and a result obtained was 30, in which 26 or 27 were assigned to pyridine rings, olefines, imine, nitriles, amide, and alkyne. Therefore, three or four aliphatic rings (cycloalkane or cycloalkene derivatives) were supposed to exist in PPP. Another calculation from the potentiometric titration of PPP in glacial acetic acid with a standard perchloric acid solution suggested the presence of three basic nitrogen atoms in one molecule of PPP. Taking account of a characteristic behavior of dipyridyl which acts as one basic nitrogen, two other basic nitrogen atoms (amine or imine) were supposed to exist at adjacent positions with pyridine rings.

Figure 5 shows one model of the possible chemical structure which was consistent with all the analytical informations presented in this paper. Although its molecular formula, $C_{54}H_{50}N_{10}O_2$, was not accurately coincided with that of the film polymer, $C_{54}H_{48}N_{10}O_2$, given in Table II, no appreciable misinterpretation would be resulted in terms of the characteristic presence of the nitrogen-containing polar functional groups and the carbon skeleton. It should be further mentioned that all the NMR spectral data were based on the acetone extract, from which a small peak of $CH_3CO\cdot$ fragment, $m/z = 43$, was detected in mass spectrum, so that one methyl group was finally dropped out of Table IV in drawing the chemical structure of the intact film polymer (Fig. 5). Such adjustment was helpful in explaining the data in Table II, while practically no alteration was needed for understanding the hydrophilic property of the given polymer.

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